Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Bromonium salts: Diaryl-λ^3-bromanes as halogen-bonding organocatalysts

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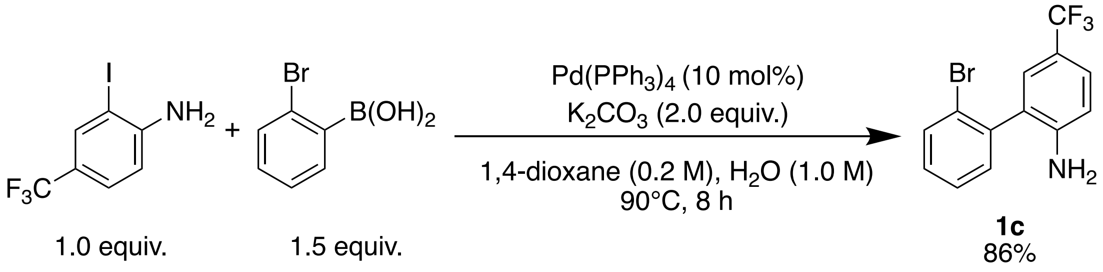
1. General Information

^{1}H-, ^{13}C-NMR spectra were recorded with JEOL JMN ECS400 FT NMR, JNM ECA500 FT NMR, Bruker AVANCE III-400M (^{1}H-NMR 400, 500 MHz, ^{13}C-NMR 100 or 125 MHz, ^{19}F-NMR 376 MHz). ^{1}H-NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CHCl_3$ at 7.26 ppm or tetramethylsilane at 0 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). ^{13}C-NMR spectra reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. CF_3CO_2H used as external standards for ^{19}F. ESI-MS spectra were obtained with Thermo Fisher, Exactive. FT-IR spectra were recorded on a JASCO FT-IR system (FT/IR-460 Plus). Mp was measured with AS ONE ATM-02. Column chromatography on SiO_2 and neutral SiO_2 was performed with Kanto Silica Gel 60 (40-50 μm). All reactions were carried out under Ar atmosphere unless otherwise noted. Commercially available organic and inorganic compounds were used without further purification. All dehydrated solvents were purchased from Wako Pure Chemical Industries, Ltd. or Nacalai Tesque, Inc., and were used without further purification. Indoles **5** were purchased from the commercial source.

2. Synthesis of catalysts

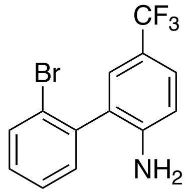
1a,[1] **1b**,[2] **2a**,[3] **3a**,[3] **3a'**[4] were synthesized according to the reported procedure.

Synthesis of 1c.



2-Iodo-4-(trifluoromethyl)aniline (1.0 equiv.), 2-bromophenylboronic acid (1.5 equiv.), $Pd(PPh_3)_4$ (10 mol%), and K_2CO_3 (2.0 equiv.) were added 1,4-dioxane (0.2 M) and H_2O (1.0 M), which was stirred for 8 hours at 90 ºC. The reaction was quenched by the addition of H_2O and extracted with CH_2Cl_2, dried over Na_2SO_4 and filtered. After the removal of solvent by evaporation, the reaction mixture was purified by column chromatography (Silica-gel, hexane/$CHCl_3$) to give **1c**.

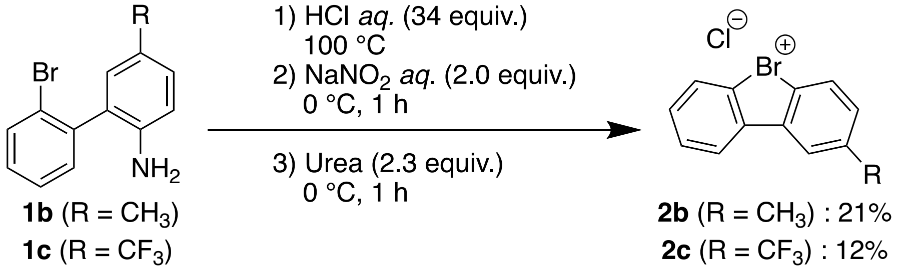
2'-bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (1c)



1c

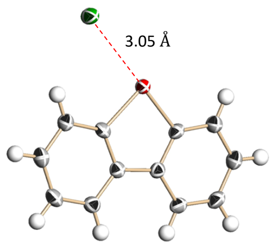
Colorless oil, 2.0 g, 6.3 mmol, 86%;
^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 7.71 (dd, J = 8.0, 1.2 Hz, 1H), 7.39-7.45 (m, 2H), 7.26-7.33 (m, 3H), 6.80 (d, J = 8.4 Hz, 1H), 3.84 (brs, 2H); ^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 146.58, 138.46, 133.30, 131.70, 129.81, 128.04, 127.62 (q, J = 3.7 Hz), 126.27 (q, J = 3.7 Hz), 126.15, 124.70 (q, J = 272 Hz), 124.01, 119.88 (q, J = 32.8 Hz), 114.71; ^{19}F-NMR (377 MHz, CHLOROFORM-D) δ -61.03; HRMS (ESI$^-$ in MeOH) calcd for $C_{13}H_8BrF_3N^-$ [M-H] 313.9798 found 313.9810; IR (Neat) ν 3494, 3397, 3054, 1626, 1514, 1337, 1111, 1076, 757, 621 cm^{-1}.

Synthesis of 2b and 2c.



Aniline derivatives **1** (1.0 equiv.) was added 10 % HCl *aq.* (34 equiv.) and heated at 100 ºC for 5 minutes the reaction was cooled to 0 ºC and $NaNO_2$ (2.0 equiv.) was added and stirred for 1 hour at the same temperature. Then, urea (2.3 equiv.) was added and stirring was continued for 1 hour at 0 ºC, after that the reaction was heated at 100 ºC for 5 minutes. The reaction was quenched by the addition of H_2O and cooled to 0 ºC to form white precipitate, which was filtered and washed by H_2O and diethyl ether, dried under the reduced pressure to give **2**.

Single crystal X-ray structure analysis of 2a.



Single crystal of **2a** was obtained by recrystallization from mixture of hexane/CH_2Cl_2.

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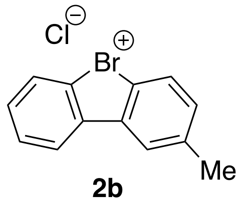
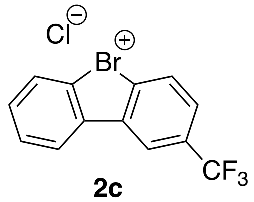
2-methyldibenzo[*b*,*d*]bromol-5-ium chloride (2b)



2b

White solid, Melting point >250 °C, 0.036 g, 0.13 mmol, 21%; ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 9.35 (d, J = 7.5 Hz, 1H), 9.20 (d, J = 8.5 Hz, 1H), 8.08 (dd, J = 7.8, 1.5 Hz, 1H), 7.90 (d, J = 1.0 Hz, 1H), 7.76 (td, J = 7.5, 1.0 Hz, 1H), 7.65-7.69 (m, 1H), 7.48 (dd, J = 8.5, 1.5 Hz, 1H), 2.57 (s, 3H); ^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 141.36, 139.00, 136.00, 135.26, 135.11, 132.17, 130.99, 130.58, 127.72, 127.19, 124.74, 124.29, 21.39; HRMS (ESI$^+$ in MeOH) calcd for $C_{13}H_{10}Br^+$ [M-Cl] 244.9966 found 244.9960; IR (KBr) ν 3048, 1574, 1429, 1139, 984, 863, 769, 715, 579, 415 cm^{-1}.

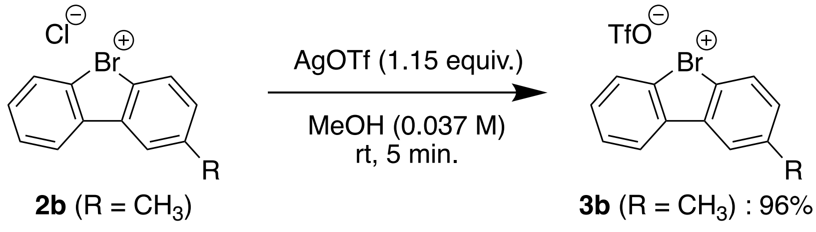
2-(trifluoromethyl)dibenzo[*b*,*d*]bromol-5-ium chloride (2c)



2c

White powder, Melting point 242 °C, 0.19 g, 0.57 mmol, 12%; ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 9.68 (d, J = 8.8 Hz, 1H), 9.49 (dd, J = 8.5, 1.5 Hz, 1H), 8.35 (d, J = 1.6 Hz, 1H), 8.20 (dd, J = 7.8, 1.5 Hz, 1H), 7.92 (dd, J = 8.8, 1.6 Hz, 1H), 7.85 (td, J = 7.8, 1.5 Hz, 1H), 7.76-7.80 (m, 1H); ^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 140.94, 139.64, 136.27, 134.03, 133.53 (q, J = 33.7 Hz), 132.13, 131.04, 129.01, 128.08, 127.42 (q, J = 3.7 Hz), 124.73, 123.14 (q, J = 274.7 Hz), 121.31 (q, J = 3.7 Hz); ^{19}F-NMR (377 MHz, CHLOROFORM-D) δ -62.47; HRMS (ESI$^+$ in MeOH) calcd for $C_{13}H_7BrF_3^+$ [M-Cl] 298.9678 found 298.9672; IR (KBr) ν 2963, 1416, 1340, 1262, 1109, 1069, 889, 798, 767, 638 cm^{-1}.

Synthesis of 3.

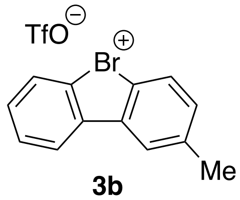


2b (R = CH_3)
2c (R = CF_3)

3b (R = CH_3) : 96%
3c (R = CF_3) : 93%

The mixture of bromonium salt **2** (1.0 equiv.) in MeOH (0.037 M) was added AgOTf (1.15 equiv.) and stirred for 5 minutes at room temperature. The product was filtered and the residue was washed with MeOH, the filtrate was evaporated and dried to give pure **3**.

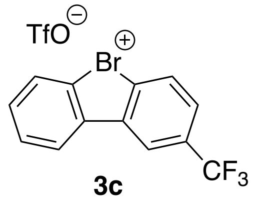
2-methyldibenzo[*b*,*d*]bromol-5-ium trifluoromethanesulfonate (3b)



3b

Gray solid, Melting point 191-193 °C, 0.14 g, 0.35 mmol, 96%; ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.53 (dd, J = 8.7, 0.9 Hz, 1H), 8.39 (d, J = 8.8 Hz, 1H), 8.15 (dd, J = 7.5, 1.5 Hz, 1H), 7.97 (d, J = 1.5 Hz, 1H), 7.85 (td, J = 7.5, 0.9 Hz, 1H), 7.72-7.77 (m, 1H), 7.56 (dd, J = 8.8, 1.5 Hz, 1H), 2.60 (s, 3H); ^{13}C-NMR (101 MHz, DMSO-D$_6$) δ 141.59, 136.73, 135.29, 135.24, 133.62, 132.57, 131.72, 131.20, 126.42, 126.14, 125.59, 125.03, 120.65 (q, J = 324.2 Hz), 20.76; ^{19}F-NMR (377 MHz, CHLOROFORM-D) δ -78.17; HRMS (ESI$^+$ in MeOH) calcd for $C_{14}H_{10}Br^+$ [M-OTf] 244.9960 found 244.9958; IR (KBr) ν 3100, 1577, 1431, 1258, 1165, 1030, 758, 637, 577, 414 cm^{-1}.

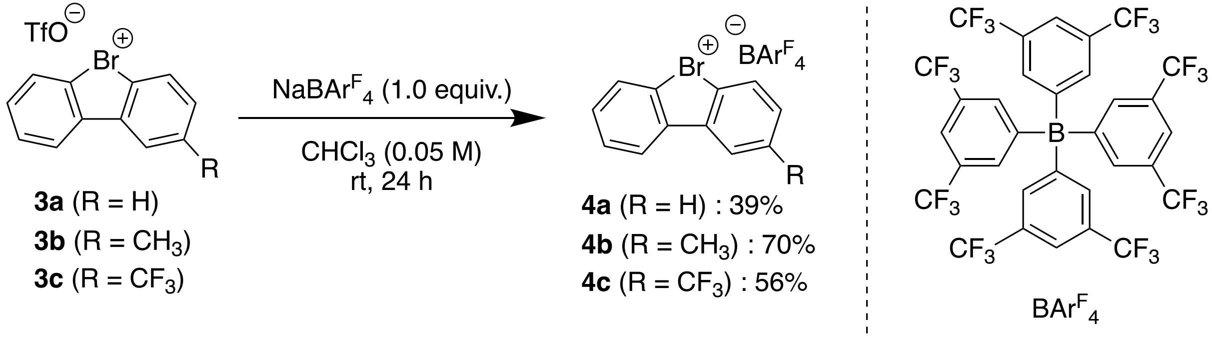
2-(trifluoromethyl)dibenzo[*b*,*d*]bromol-5-ium trifluoromethanesulfonate (3c)



3c

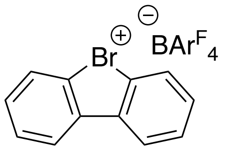
Gray solid, Melting point 203-205 °C, 0.13 g, 0.28 mmol, 93%; ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.87 (d, J = 9.4 Hz, 1H), 8.70 (dd, J = 8.7, 0.9 Hz, 1H), 8.41 (d, J = 1.6 Hz, 1H), 8.27 (dd, J = 7.8, 1.6 Hz, 1H), 8.02 (dd, J = 9.4, 1.9 Hz, 1H),7.93(ddd, J = 7.8, 7.3, 0.9 Hz, 1H), 7.86 (ddd, J = 8.7, 7.3, 1.9 Hz, 1H); ^{13}C-NMR (101 MHz, DMSO-D$_6$) δ 139.41, 137.48, 136.83, 134.46, 132.67, 131.80 (q, J = 32.3 Hz), 131.32, 128.15-128.03 (m), 127.13, 126.91, 125.53, 123.52-123.45 (m), 123.47 (q, J = 273.6 Hz),120.67 (q, J = 322.0 Hz); ^{19}F-NMR (377 MHz, CHLOROFORM-D) δ -62.67, -78.15; HRMS (ESI$^+$ in MeOH) calcd for $C_{13}H_7BrF_3^+$ [M-OTf] 298.9678 found 298.9671; IR (KBr) ν 3103, 1416, 1341, 1255, 1173, 1026, 826, 766, 632, 432 cm^{-1}.

Synthesis of 4.



Bromonium salt **3** was dissolved in CHCl$_3$ (0.05 M) and NaBAr$^F{}_4$ (1.0 equiv.) was added. The reaction was stirred until the clear solution formed (for 24 hours). Then, the reaction was filtered and the filtrate was evaporated to give crude product, which was purified by recrystallization (CHCl$_3$/hexane). Finally, the product was filtered and dried to give **4**.

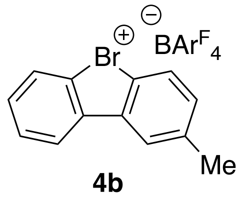
dibenzo[*b*,*d*]bromol-5-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (4a)



4a

White solid, Melting point 135-138 °C, 0.033 g, 0.031 mmol, 39%; ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.17 (dd, J = 7.9, 1.4 Hz, 2H), 7.87-7.91 (m, 2H), 7.68-7.75 (m, 12H), 7.48 (s, 4H); ^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 161.70 (dd, J = 99.8, 49.9 Hz), 136.74, 134.75, 134.69, 133.47, 132.67, 129.67-128.59 (m), 127.30, 124.38 (q, J = 272.7 Hz) 124.04, 117.59-117.56 (m); ^{19}F-NMR (377 MHz, CHLOROFORM-D) δ -62.33; HRMS (ESI$^+$ in MeOH) calcd for $C_{12}H_8Br^+$ [M-BAr$^F{}_4$] 230.9804 found 230.9802; IR (KBr) ν 3104, 1611, 1449, 1355, 1276, 1120, 888, 839, 744, 683 cm^{-1}.

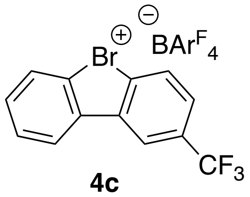
2-methyldibenzo[*b*,*d*]bromol-5-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (4b)



4b

Gray solid, Melting point 156-158 °C, 0.12 g, 0.11 mmol, 70%; ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.14-8.16 (m, 1H), 7.99 (d, J = 1.3 Hz, 1H), 7.84-7.88 (m, 1H), 7.72 (d, J = 1.9 Hz, 8H), 7.65-7.69 (m, 2H), 7.52-7.56 (m, 1H), 7.48-7.51 (m, 5H), 2.57 (s, 3H); ^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 161.69 (dd, J = 99.4, 49.9 Hz), 144.40, 137.02, 134.76, 134.68, 134.58, 134.48, 133.78, 133.32, 132.61, 129.54-128.55 (m), 127.62, 127.23, 124.38 (q, J = 272.2 Hz) 124.00, 123.32, 117.59-117.51 (m), 21.27; ^{19}F-NMR (377 MHz, CHLOROFORM-D) δ -62.34; HRMS (ESI$^+$ in MeOH) calcd for $C_{13}H_{10}Br^+$ [M-BAr$^F{}_4$] 244.9960 found 244.9956; IR (KBr) ν 3093, 1611, 1355, 1285, 1119, 889, 839, 794, 716, 683 cm^{-1}.

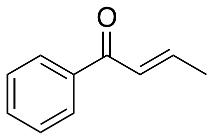
2-(trifluoromethyl)dibenzo[*b*,*d*]bromol-5-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (4c)

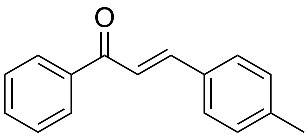


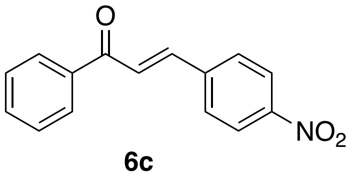
4c

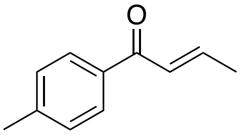
White solid, Melting point 130-131 °C, 0.058 g, 0.050 mmol, 56%; ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.47 (d, J = 2.1 Hz, 1H), 8.31 (dd, J = 8.0, 2.1 Hz, 1H), 7.94-8.00 (m, 2H), 7.74-7.80 (m, 10H), 7.61 (d, J = 8.5 Hz, 1H), 7.49 (s, 4H); ^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 161.73 (dd, J = 99.8, 49.9 Hz), 137.86, 137.60, 135.88, 134.77, 134.66, 133.32, 133.16, 130.17-130.07 (m), 129.69-128.70 (m), 127.87, 124.86, 124.40-124.26 (m), 124.32 (q, J = 272.2 Hz), 124.02, 122.04 (q, J = 274.7 Hz), 117.67-117.61 (m) (One carbon peak is overrapped with other peak); ^{19}F-NMR (377 MHz, CHLOROFORM-D) δ -62.31, -62.97; HRMS (ESI$^+$ in MeOH) calcd for $C_{13}H_7BrF_3$ [M-BArF$_4^-$] 298.9683 found 298.9676; IR (KBr) ν 3092, 1611, 1356, 1280, 1137, 889, 839, 754,716, 669 cm^{-1}.

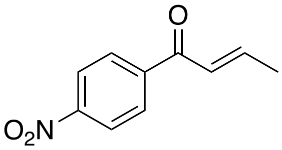
3. Syntheses of Michael acceptors.


6a


6b

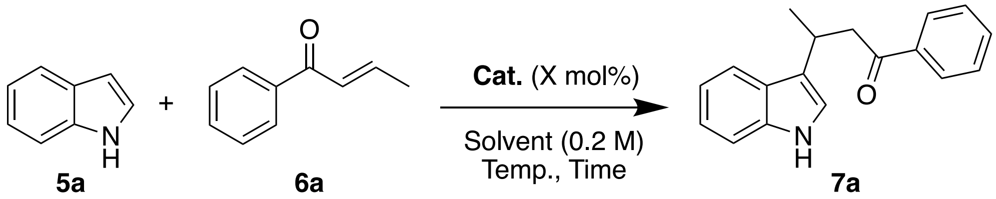

6c


6d


6e

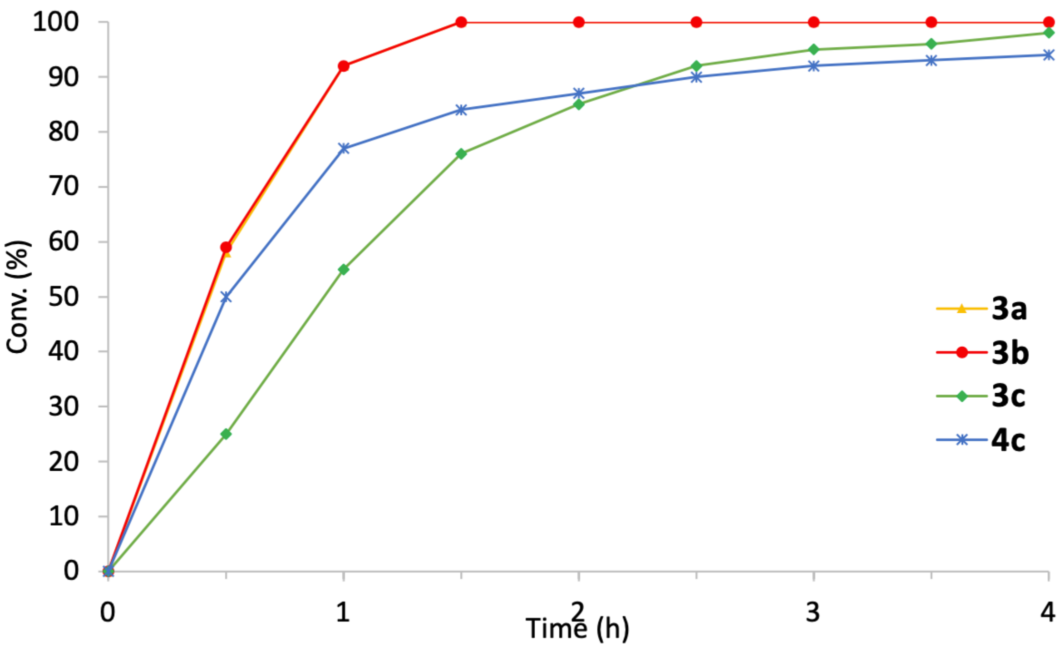
Michael acceptor **6a**,[5] **6b**,[6] **6c**,[6] **6d**,[7] and **6e**[7] were synthesized according to the reported procedure. Chalcone was purchased from TCI.

4. General procedure for the catalytic Michael addition reaction of indole 5a to enones 6a (Table 1 and 2).



Indole **5a** (1.0 equiv.), enone **6a** (1.0 equiv.), and catalyst (5 or 10 or 20 mol%) were added solvent (0.2 M) and stirred at the corresponding temperature. The reaction was monitored by TLC or ^{1}H-NMR spectroscopic analysis. After the consumption of substrate (or regulated reaction time finished), the solvent was removed by evaporation and the residue was purified by column chromatography (Silica-gel, hexane/ethyl acetate) to give **7a**.

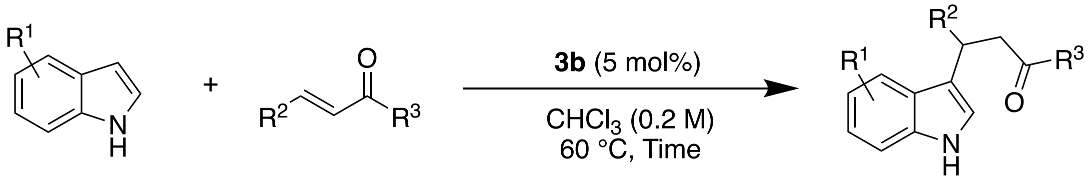
5. Time-course conversion graph of 5a in Table 2 monitored by ^{1}H NMR (Fig. S1), and their detailed data.



Catalyst Time (h)	3a	3b	3c	4c
0.5	58	59	25	50
1	92	92	55	77
1.5	100	100	76	84
2	100	100	85	87
2.5	100	100	92	90
3	100	100	95	92
3.5	100	100	96	93
4	100	100	98	94

All conversions were determined with ^{1}H-NMR

6. General procedure for the catalytic Michael addition reaction of indoles to enones (Scheme 2).

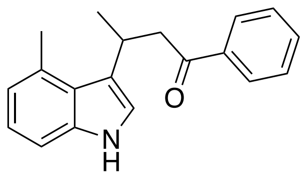


5 **6** **7**

Indole **5** (1.0 equiv.), enone **6** (1.0 equiv.), and **3b** (5 mol%) were added CHCl$_3$ (0.2 M) and stirred at 60 ºC. After the stirring of designated reaction time, the solvent was removed by evaporation and the residue was purified by column chromatography (Silica-gel, hexane/ethyl acetate) to give **7**.

The spectroscopic data of **7a**,[5] **7b**,[8] **7c**,[9] **7e**,[10] **7f**,[8] **7g**,[10] **7j**,[8] **7l**,[8] **7n**,[11] ,**7o**,[12] **7p**[13], and **7q**[14] were well matched with those of reported values.

3-(4-methyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (7d)

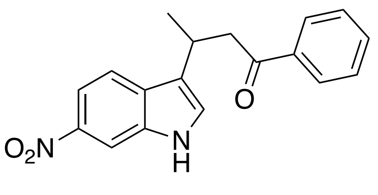


7d

Brown oil, 52.8 mg, 0.190 mmol, 63%;

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 7.99 (brs, 1H), 7.94-7.97 (m, 2H), 7.52-7.57 (m, 1H), 7.42-7.46 (m, 2H), 7.19 (d, J = 8.1 Hz, 1H), 7.02-7.08 (m, 2H), 6.84 (d, J = 7.2 Hz, 1H), 4.11-4.19 (m, 1H), 3.41 (dd, J = 16.9, 4.0 Hz, 1H), 3.21 (dd, J = 16.9, 9.4 Hz, 1H), 2.70 (s, 3H), 1.40 (d, J = 6.6 Hz, 3H); ^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 199.29, 137.26, 136.66, 132.94, 130.76, 128.53, 128.03, 124.94, 123.24, 122.05, 121.36, 119.88, 109.03, 48.04, 27.14, 22.21, 20.50; HRMS (ESI$^+$ in MeOH) calcd for $C_{19}H_{20}ON$ [M+H] 278.1539 found 278.1537; IR (Neat) ν 3466, 3398, 3011, 2964, 1680, 1595, 1448, 1337, 1216, 753 cm^{-1}.

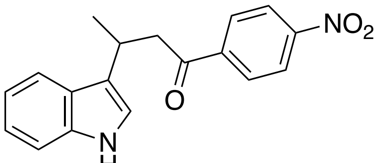
3-(6-nitro-1*H*-indol-3-yl)-1-phenylbutan-1-one (7i)



7i

Yellow oil, 72.2 mg, 0.234 mmol, 79%; ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.64 (s, 1H), 8.29 (d, J = 1.9 Hz, 1H), 7.99 (ddd, J = 8.8, 2.1, 0.6 Hz, 1H), 7.92-7.95 (m, 2H), 7.69 (d, J = 8.8 Hz, 1H), 7.54-7.58 (m, 1H), 7.42-7.47 (m, 2H), 7.33 (dd, J = 2.5, 0.6 Hz, 1H), 3.82-3.90 (m, 1H), 3.43 (dd, J = 16.6, 6.0 Hz, 1H), 3.30 (dd, J = 16.6, 7.7 Hz, 1H), 1.47 (d, J = 6.9 Hz, 3H); ^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 199.29, 143.13, 136.98, 134.81, 133.19, 131.01, 128.63, 128.03, 126.35, 122.40, 119.02, 114.73, 108.18, 46.24, 26.87, 21.36; HRMS (ESI$^+$ in MeOH) calcd for $C_{18}H_{17}O_3N_2$ [M+H] 309.1234 found 309.1230; IR (Neat) ν 3434, 3303, 2964, 2398, 1683, 1505, 1337, 1215, 1067, 756 cm^{-1}.

3-(1*H*-indol-3-yl)-1-(4-nitrophenyl)butan-1-one (7k)



7k

Yellow oil, 44.7 mg, 0.147 mmol, 88%; ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.22-8.25 (m, 2H), 8.00-8.04 (m, 2H), 7.97 (brs, 1H), 7.63-7.66 (m, 1H), 7.34-7.36 (m, 1H), 7.18-7.22 (m, 1H), 7.10-7.14 (m, 1H), 7.01 (d, J = 2.2 Hz, 1H), 3.77-3.86 (m, 1H), 3.51 (dd, J = 16.4, 5.4 Hz, 1H), 3.27 (dd, J = 16.4, 8.4 Hz, 1H), 1.48 (d, J = 6.9 Hz, 3H); ^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 198.24, 150.09, 141.62, 136.47, 129.00, 126.09, 123.69, 122.18, 120.76, 120.29, 119.39, 119.02, 111.34, 46.97, 27.26, 20.96; HRMS (ESI$^+$ in MeOH) calcd for $C_{18}H_{16}O_3N_2Na$ [M+Na] 331.1053 found 331.1049; IR (Neat) ν 3466, 3381, 2968, 1685, 1602, 1458, 1278, 1106, 1011, 859 cm^{-1}.

7. Mechanistic studies (Scheme 3).

$$\textbf{5a} \quad + \quad \textbf{6a} \quad \xrightarrow[\substack{\text{CHCl}_3\ (0.2\ \text{M}) \\ 60\ ^\circ\text{C, 4 h}}]{\substack{\textbf{3b}\ (5\ \text{mol\%}) \\ \text{Cyclohexene (2.5 mol\%)}}} \quad \underset{>99\%\ \text{Conv.}}{\textbf{7a}} \qquad (1)$$

Indole **5a** (1.0 equiv.), enone **6a** (1.0 equiv.), and **3b** (5 mol%) were added CHCl₃ (0.2 M) and Cyclohexene (2.5 mol%), which was stirred at 60 ºC. The reaction was monitored by TLC and ^{1}H-NMR spectroscopic analysis, and after 4 hours **5a** was almost completely converted to **7a**.

$$\textbf{5a} \quad + \quad \textbf{6a} \quad \xrightarrow[\substack{\text{CHCl}_3\ (0.2\ \text{M}) \\ 60\ ^\circ\text{C, 4 h}}]{\text{2-Bromobiphenyl (20 mol\%)}} \quad \underset{0\%\ \text{Conv.}}{\textbf{7a}} \qquad (2)$$

Indole **5a** (1.0 equiv.), enone **6a** (1.0 equiv.) were added CHCl₃ (0.2 M) and 2-bromobiphenyl (20 mol%), which was stirred at 60 ºC. The reaction was monitored by TLC and ^{1}H-NMR spectroscopic analysis, and after 4 hours almost no conversion of **5a** to **7a** was observed.

$$\mathbf{5a} \quad + \quad \mathbf{6a} \quad \xrightarrow[\substack{\text{CHCl}_3\text{ (0.2 M)} \\ 60\ °\text{C, 24 h}}]{\substack{\mathbf{3b}\text{ (10 mol\%)} \\ \text{TEMPO (5 mol\%)}}} \quad \underset{>99\%\text{ Conv.}}{\mathbf{7a}} \tag{3}$$

Indole **5a** (1.0 equiv.), enone **6a** (1.0 equiv.), TEMPO (5 mol%), and **3b** (10 mol%) were added $CHCl_3$ (0.2 M), which was stirred at 60 ºC. The reaction was monitored by TLC and ^{1}H-NMR spectroscopic analysis, and after 24 hours **5a** was almost completely converted to **7a**.

$$\mathbf{5a} \quad + \quad \mathbf{6a} \quad \xrightarrow[\substack{\text{CHCl}_3\text{ (0.2 M, 1.0 mL)} \\ 60\ °\text{C, 0.5 h}}]{\substack{\mathbf{3b}\text{ (10 mol\%)} \\ \text{H}_2\text{O (50 }\mu\text{L)}}} \quad \underset{8\%\text{ Conv.}}{\mathbf{7a}} \tag{4}$$

Indole **5a** (1.0 equiv.), enone **6a** (1.0 equiv.), and **3b** (10 mol%) were added $CHCl_3$ (1.0 mL, 0.2 M) and H_2O (50 µL), which was stirred at 60 ºC. The reaction was monitored by TLC and ^{1}H-NMR spectroscopic analysis, and after 0.5 hours **5a** was converted to **7a** in only 8 %.

References

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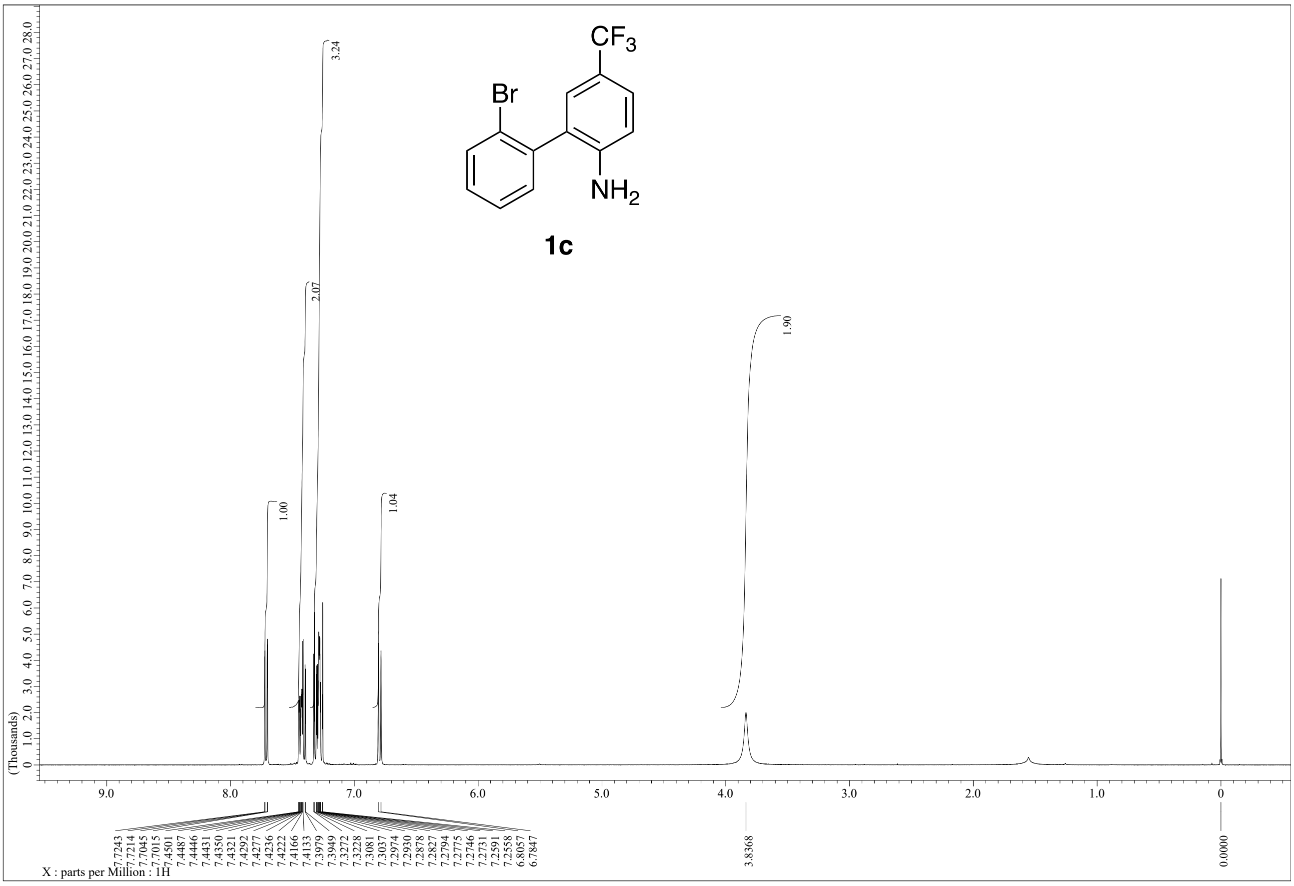
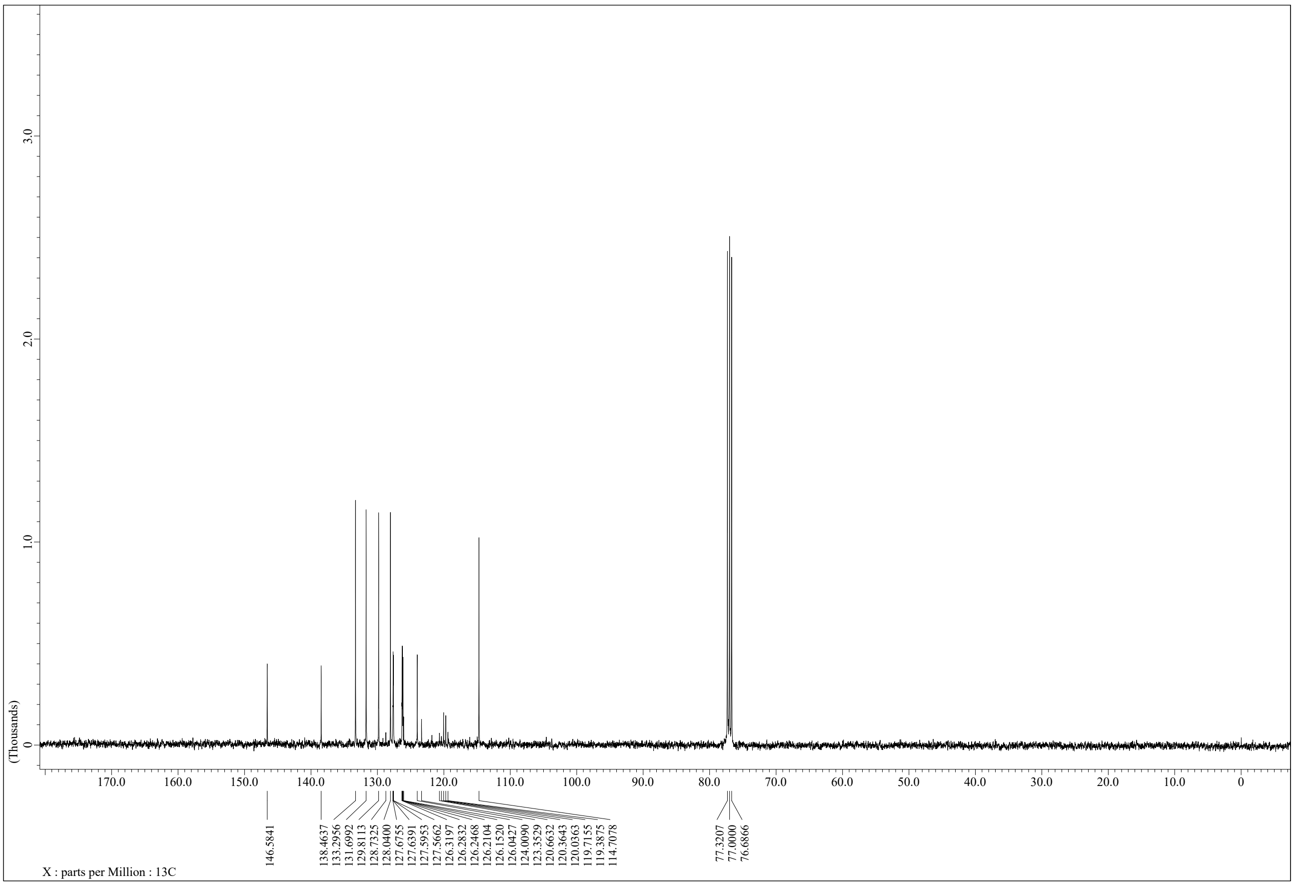
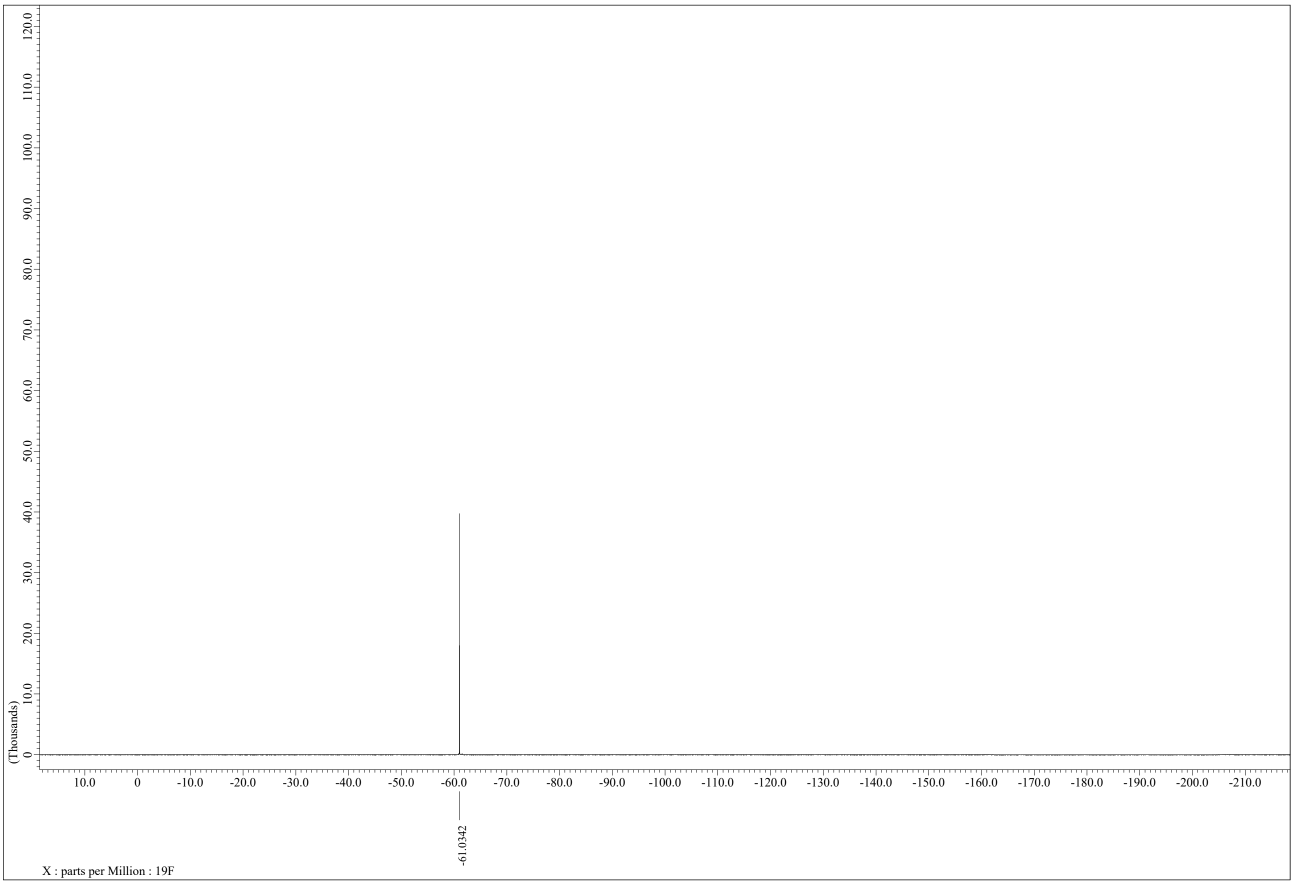
8. ^{1}H-, ^{13}C-, and ^{19}F-NMR spectra.



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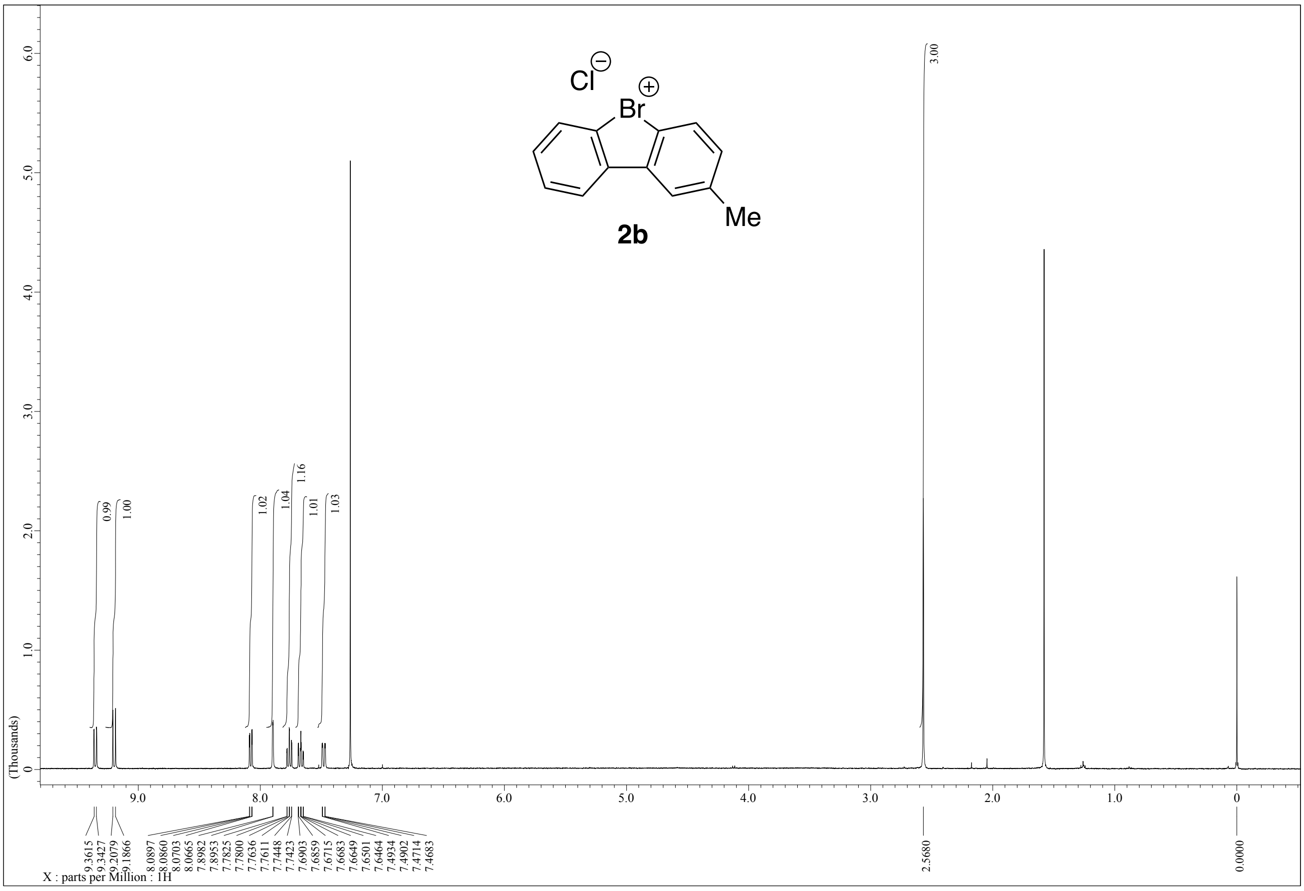
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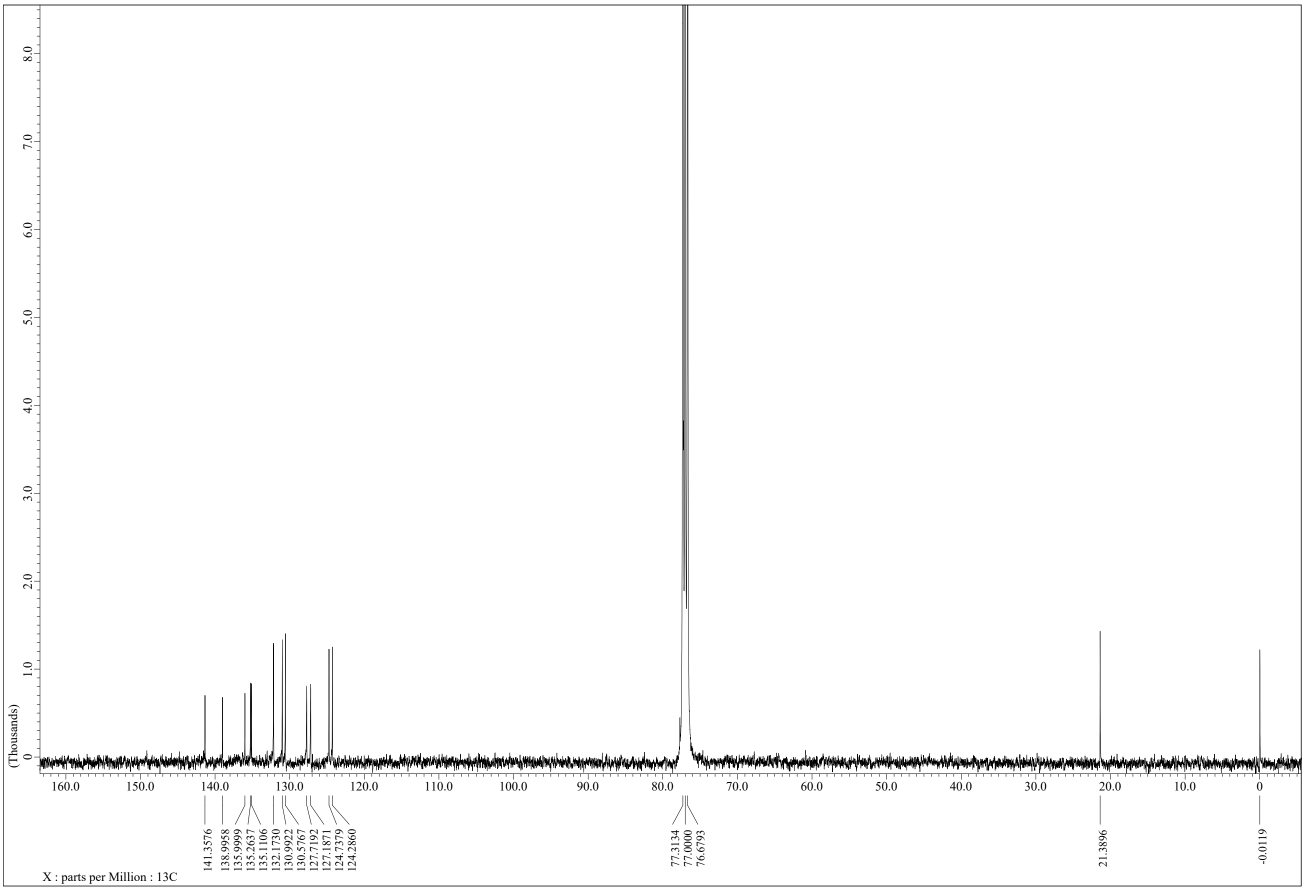
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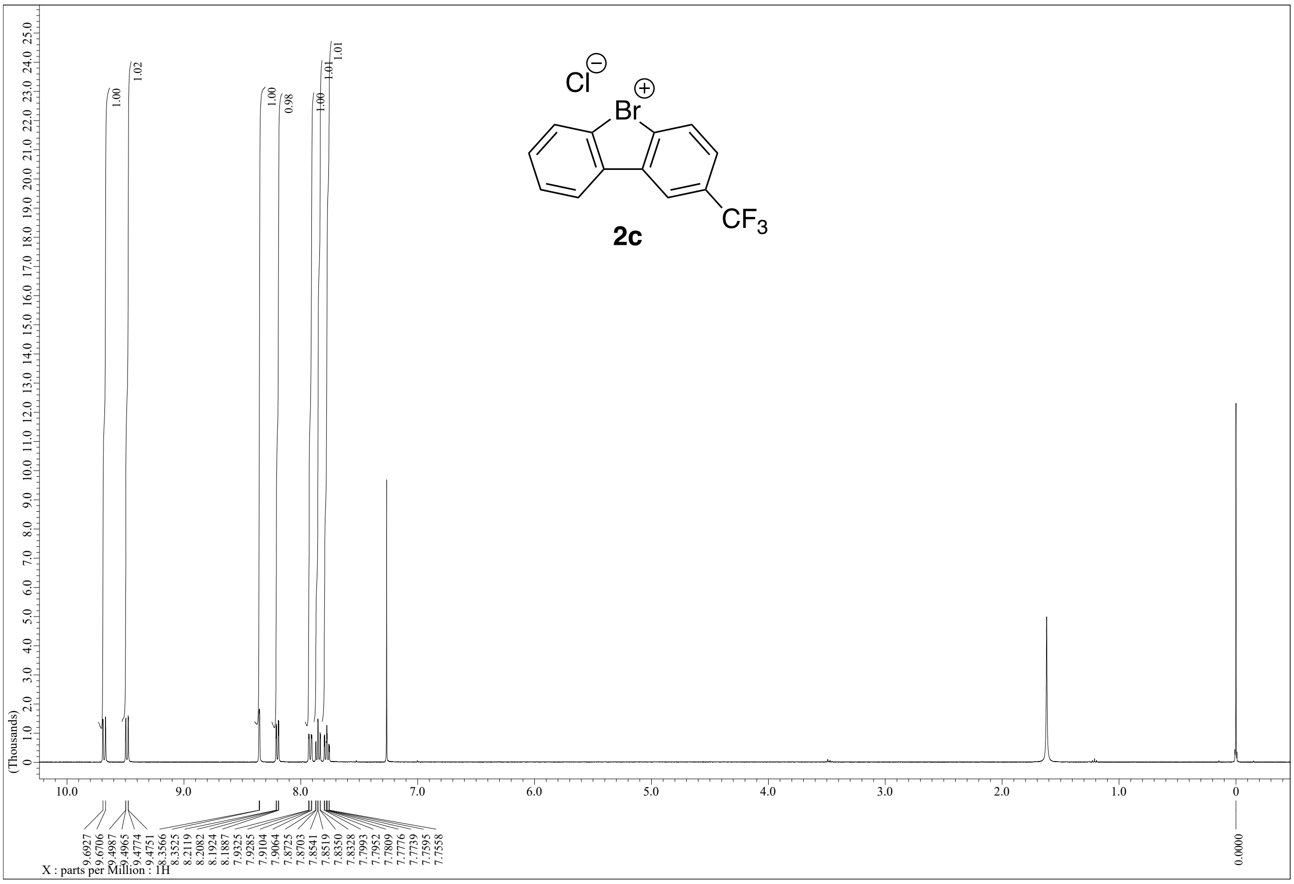

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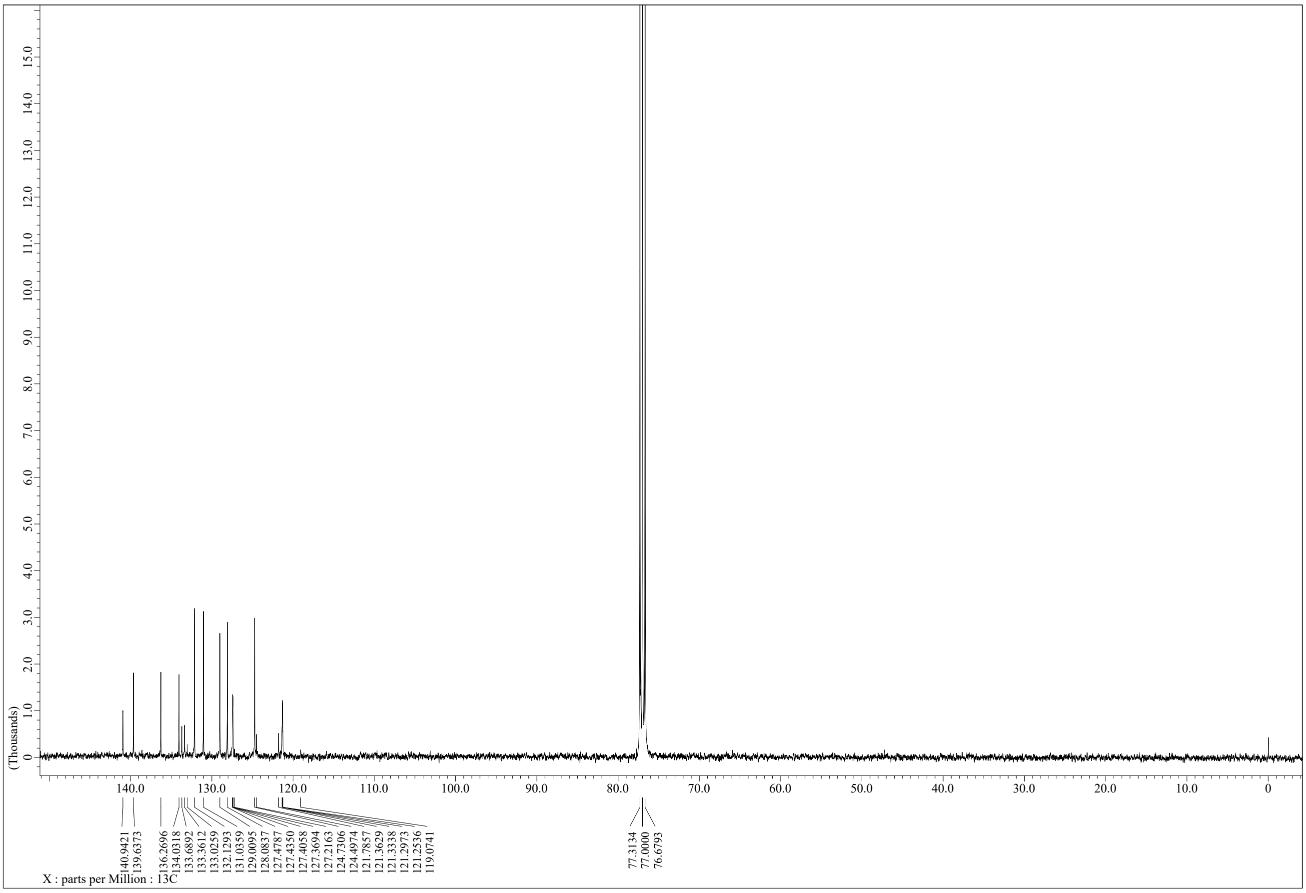

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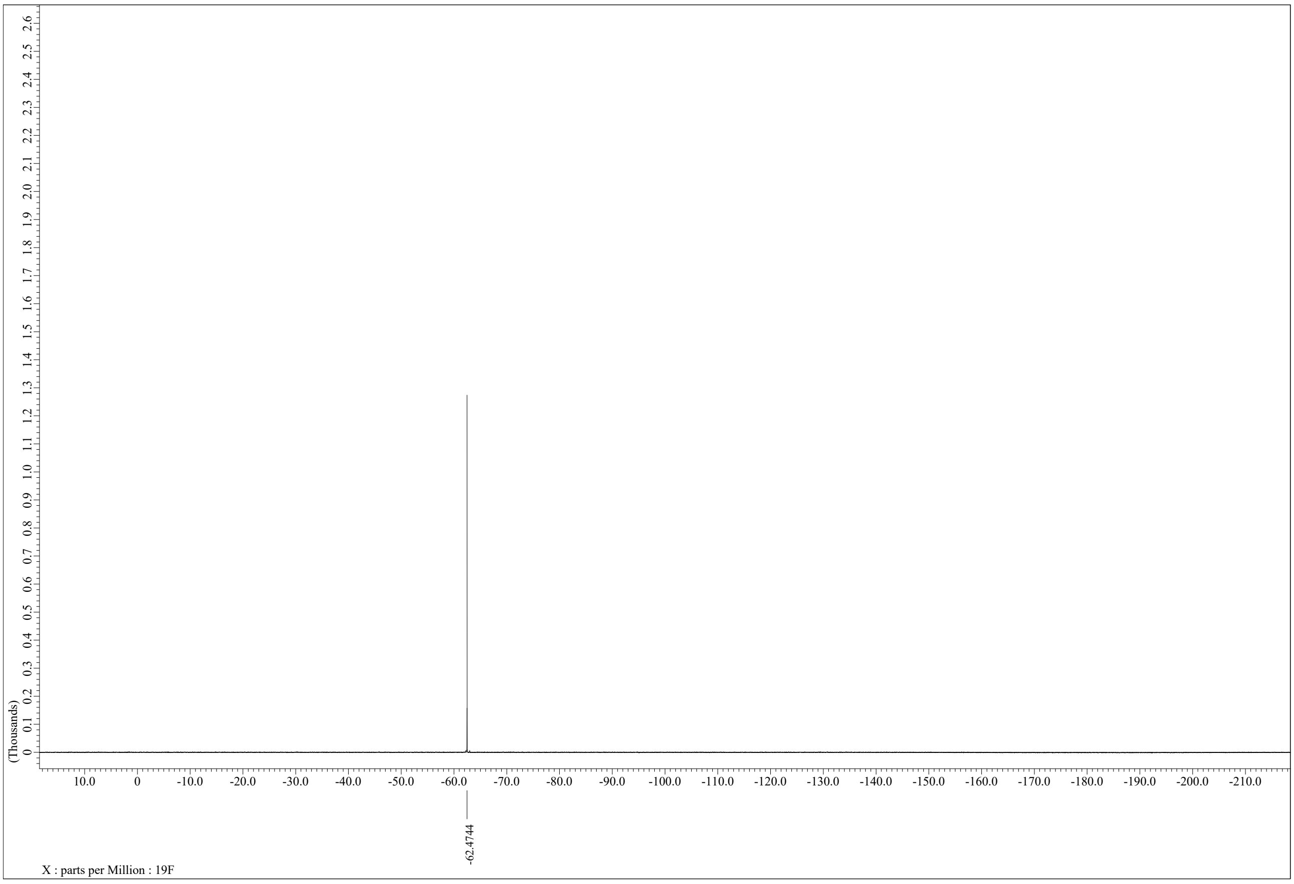
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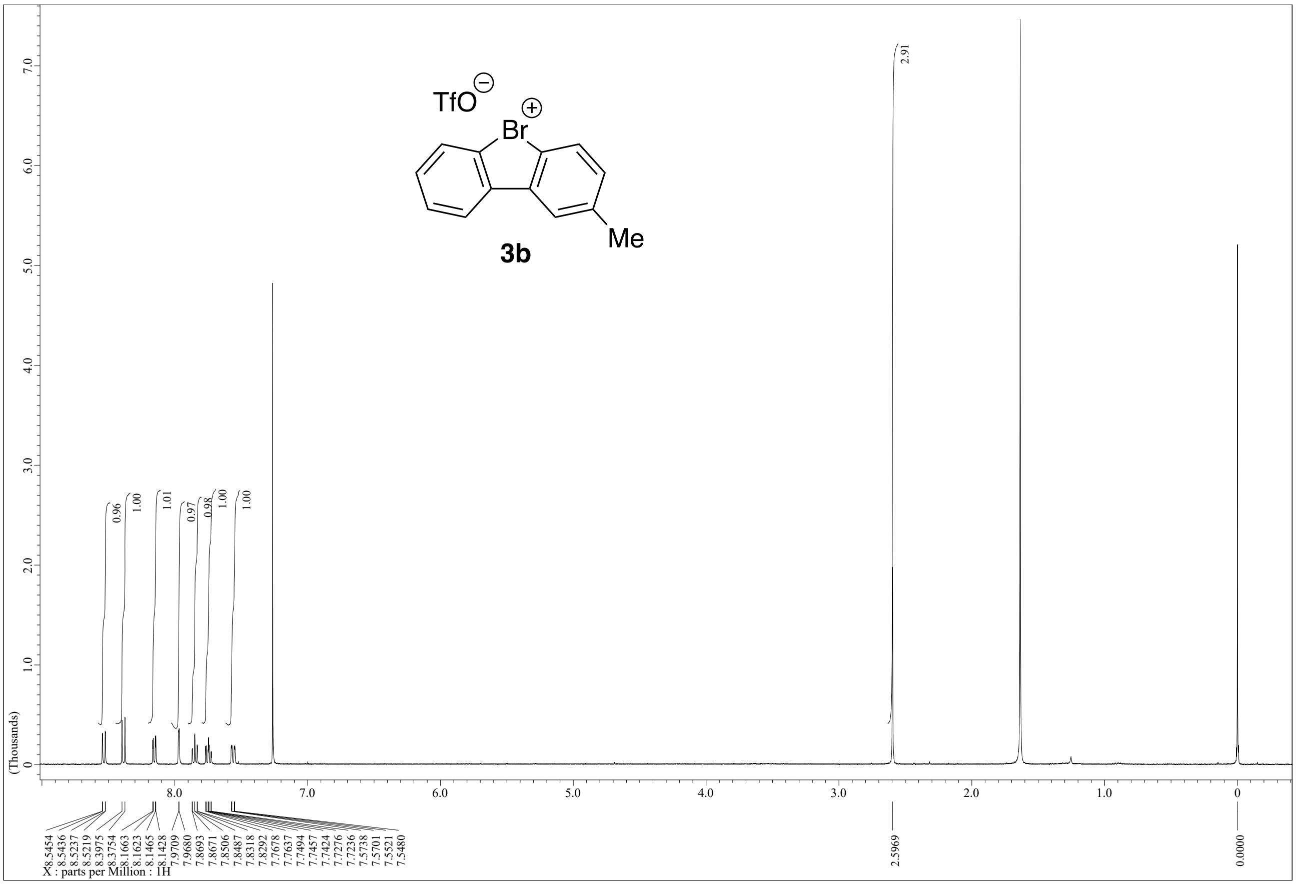
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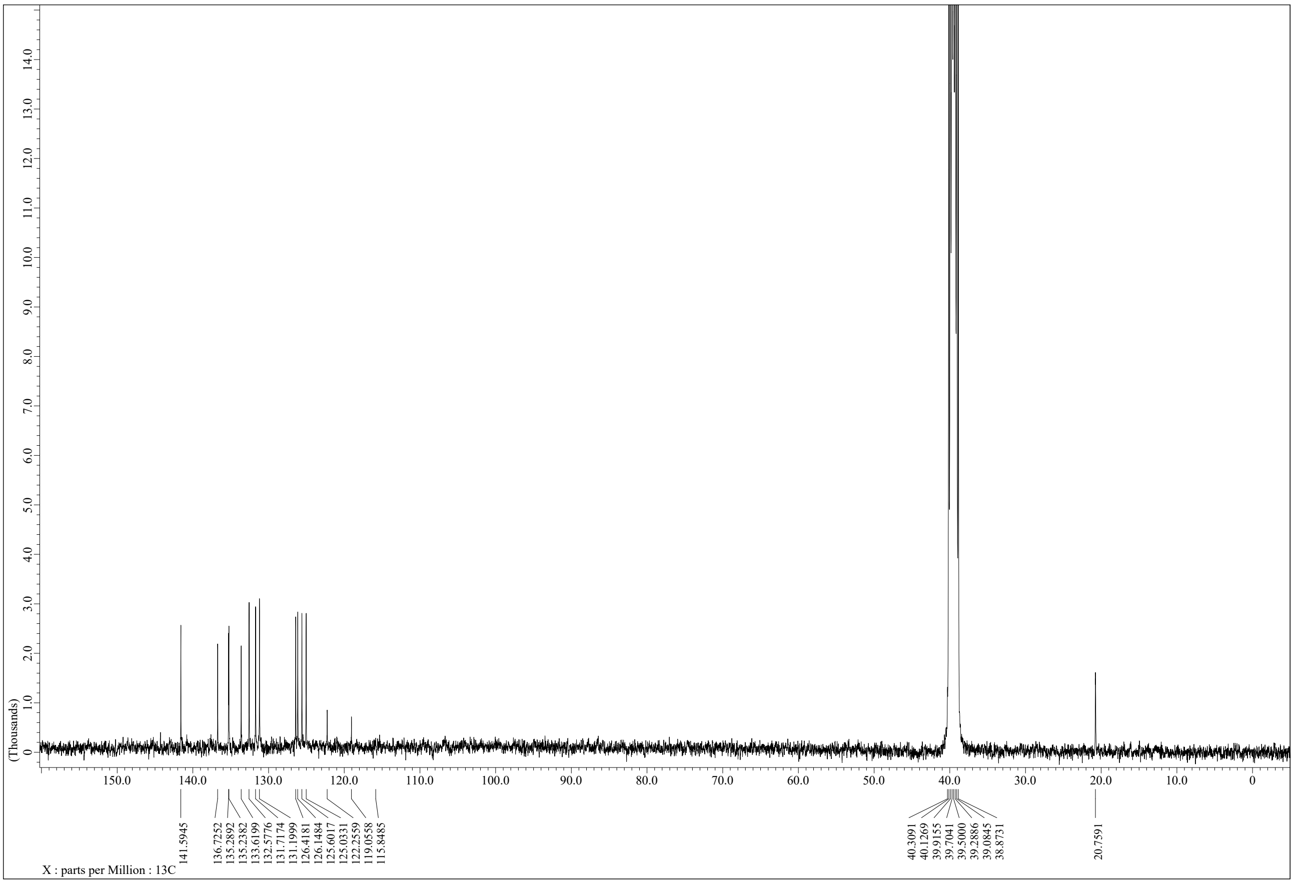
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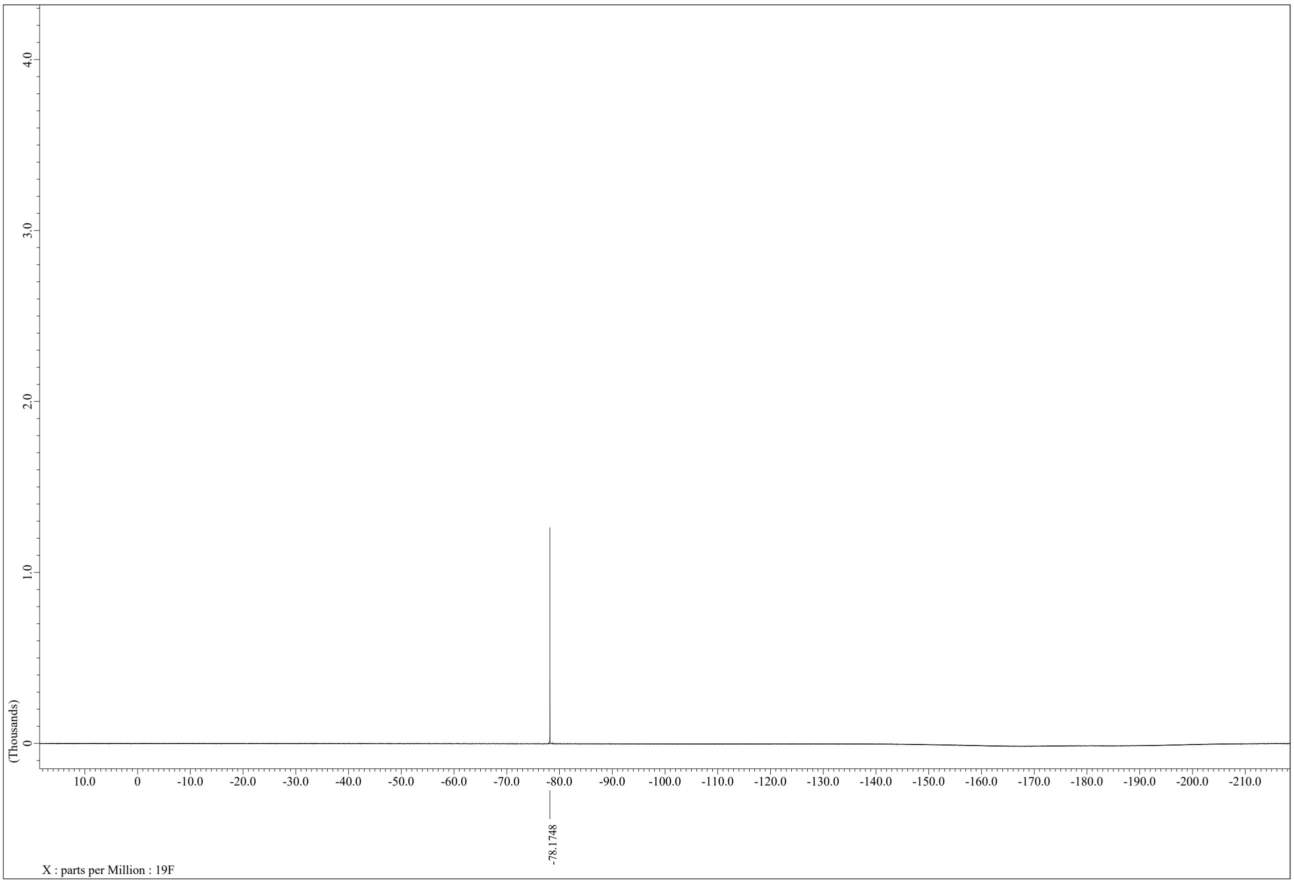
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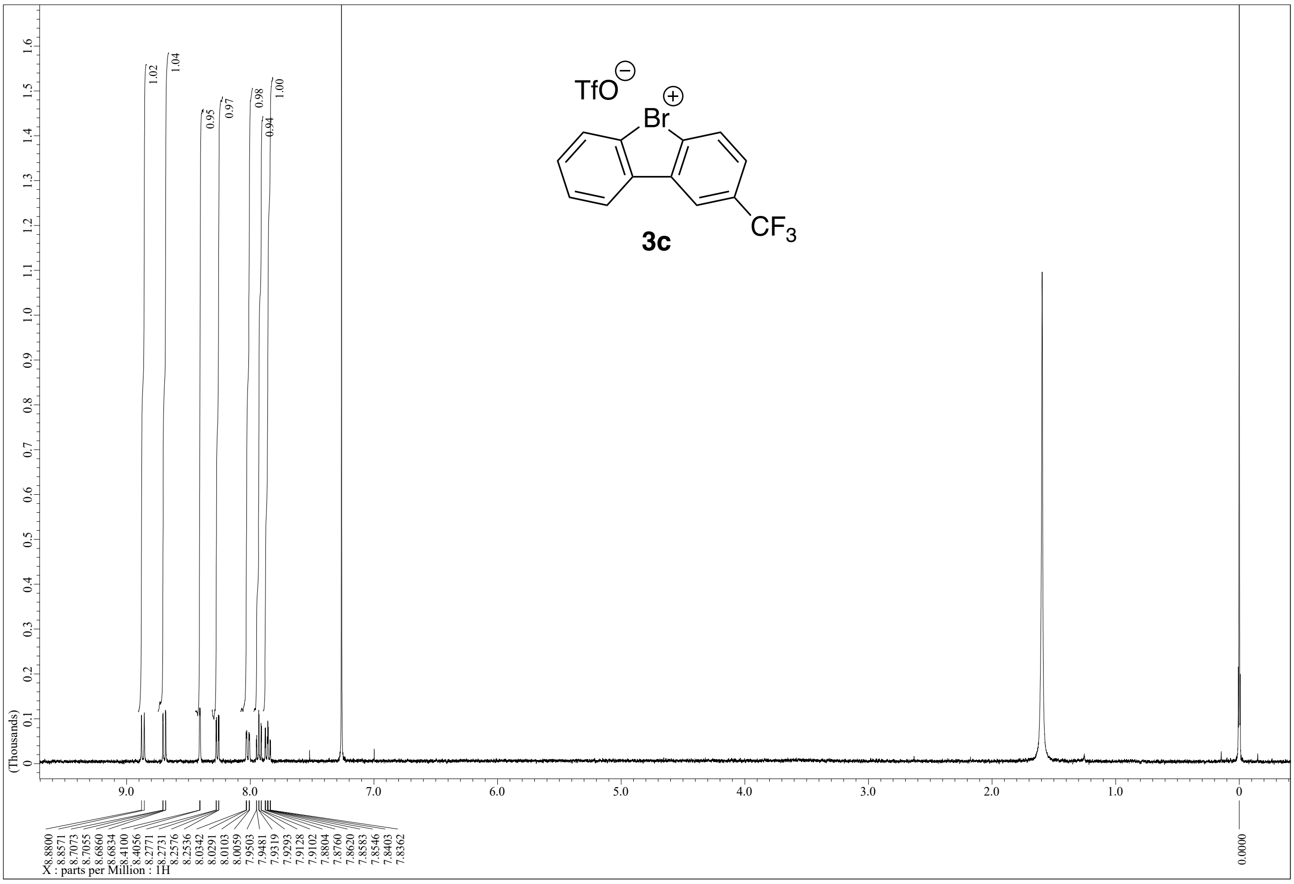
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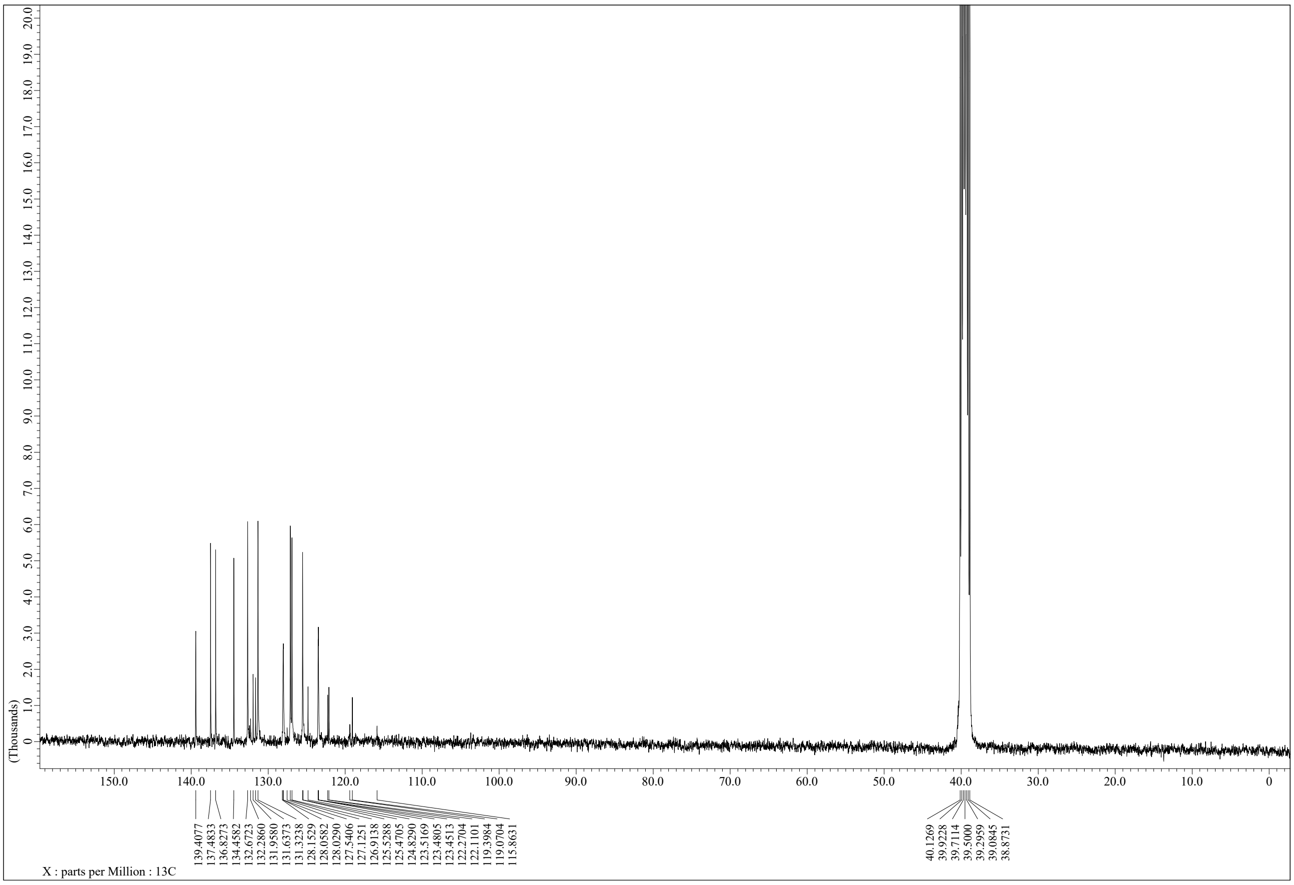
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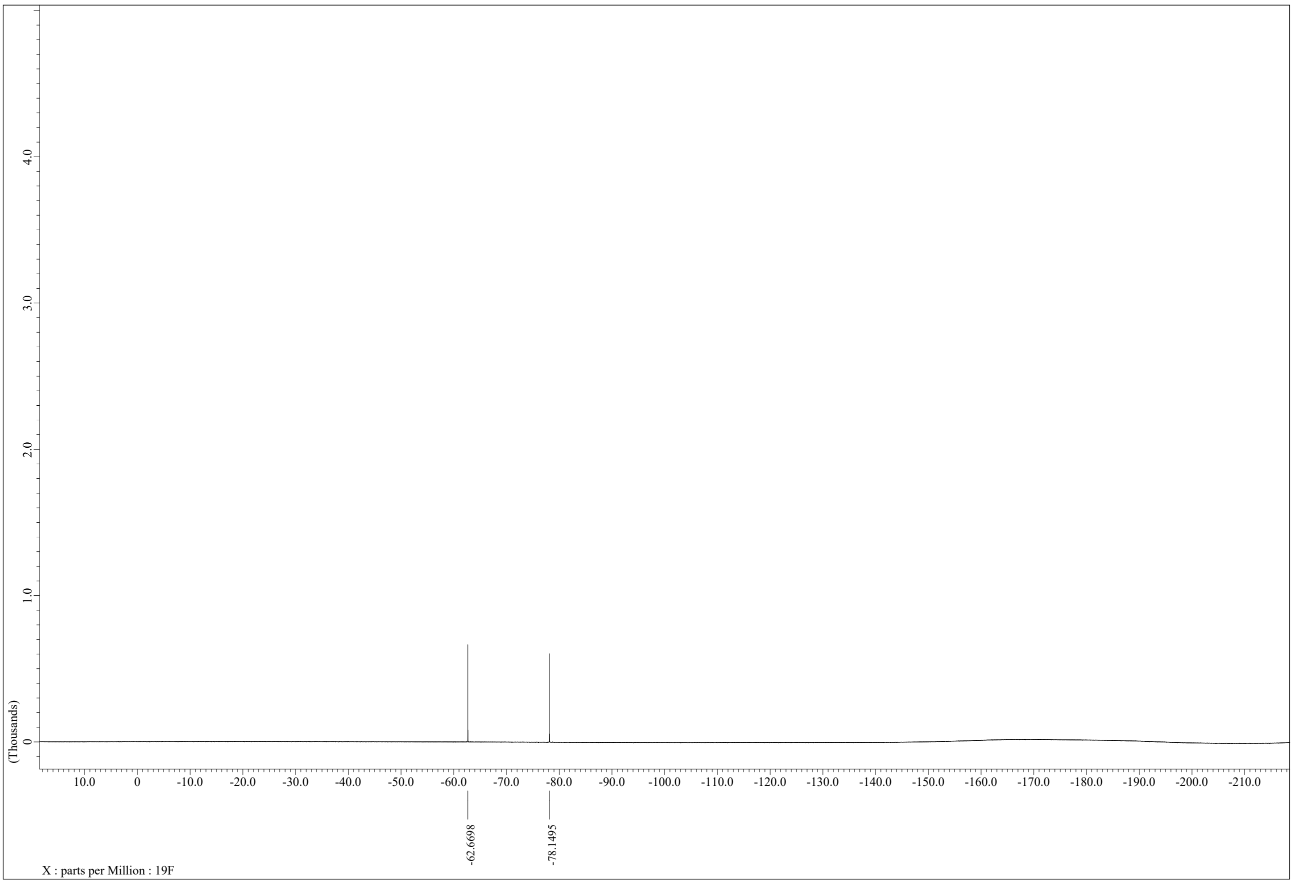

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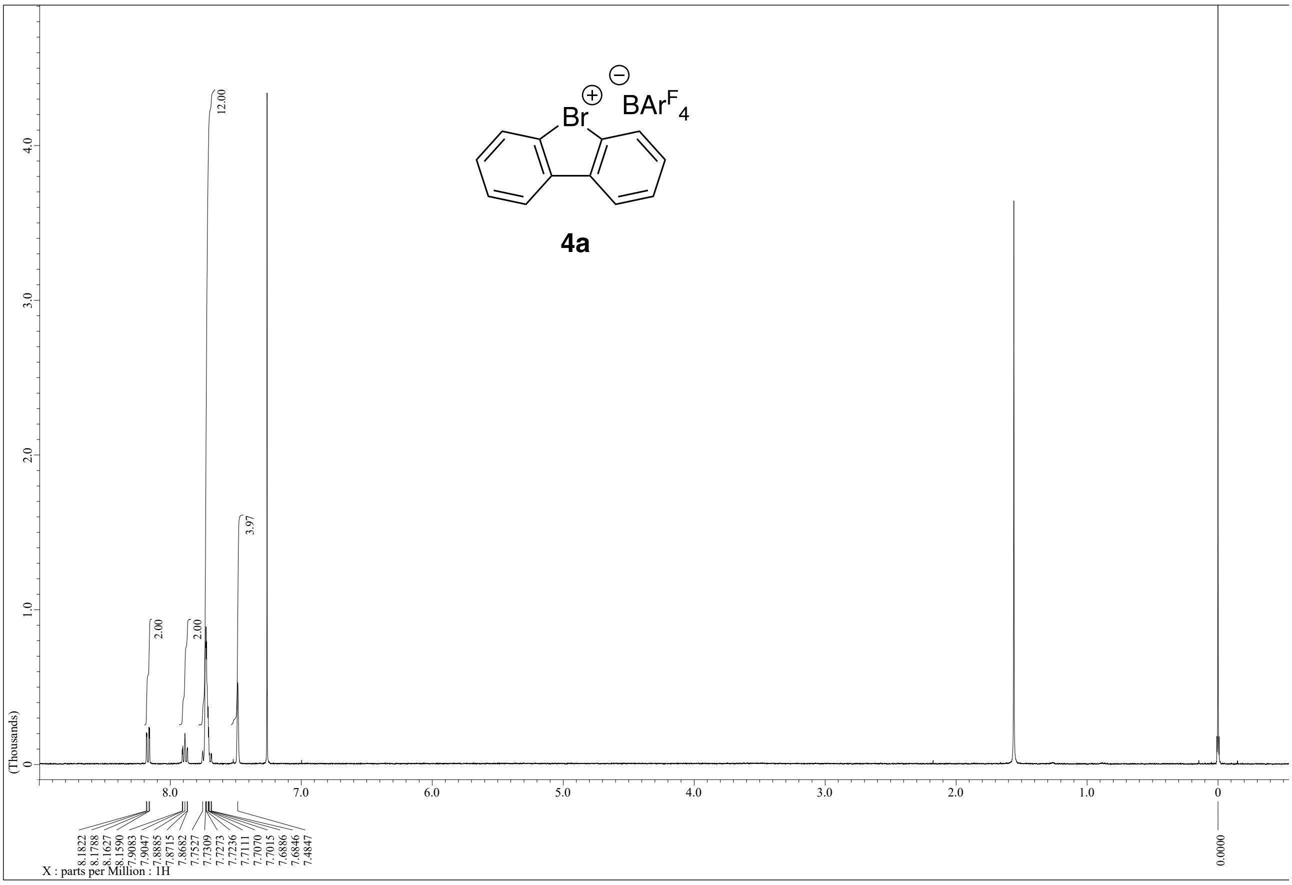
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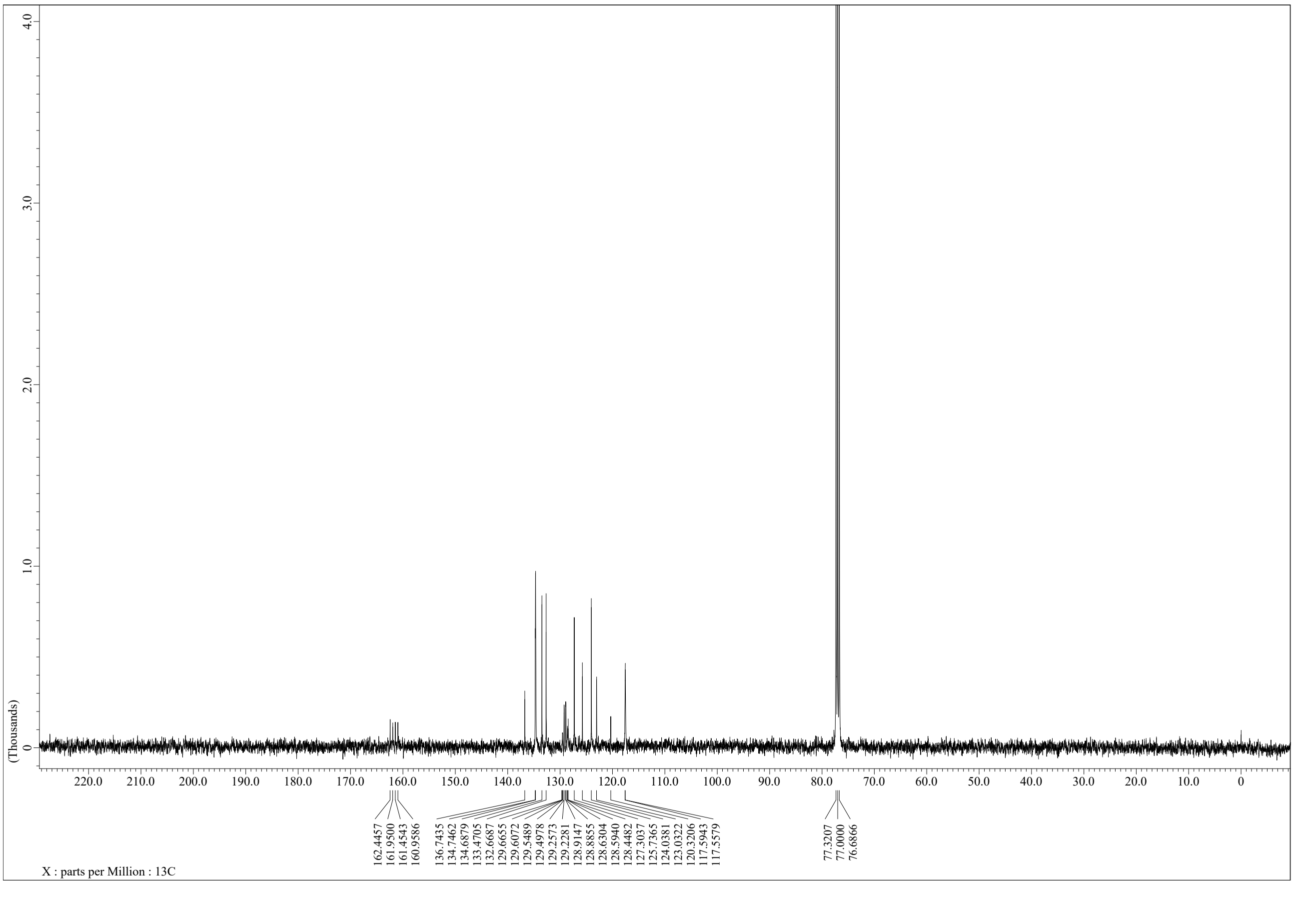
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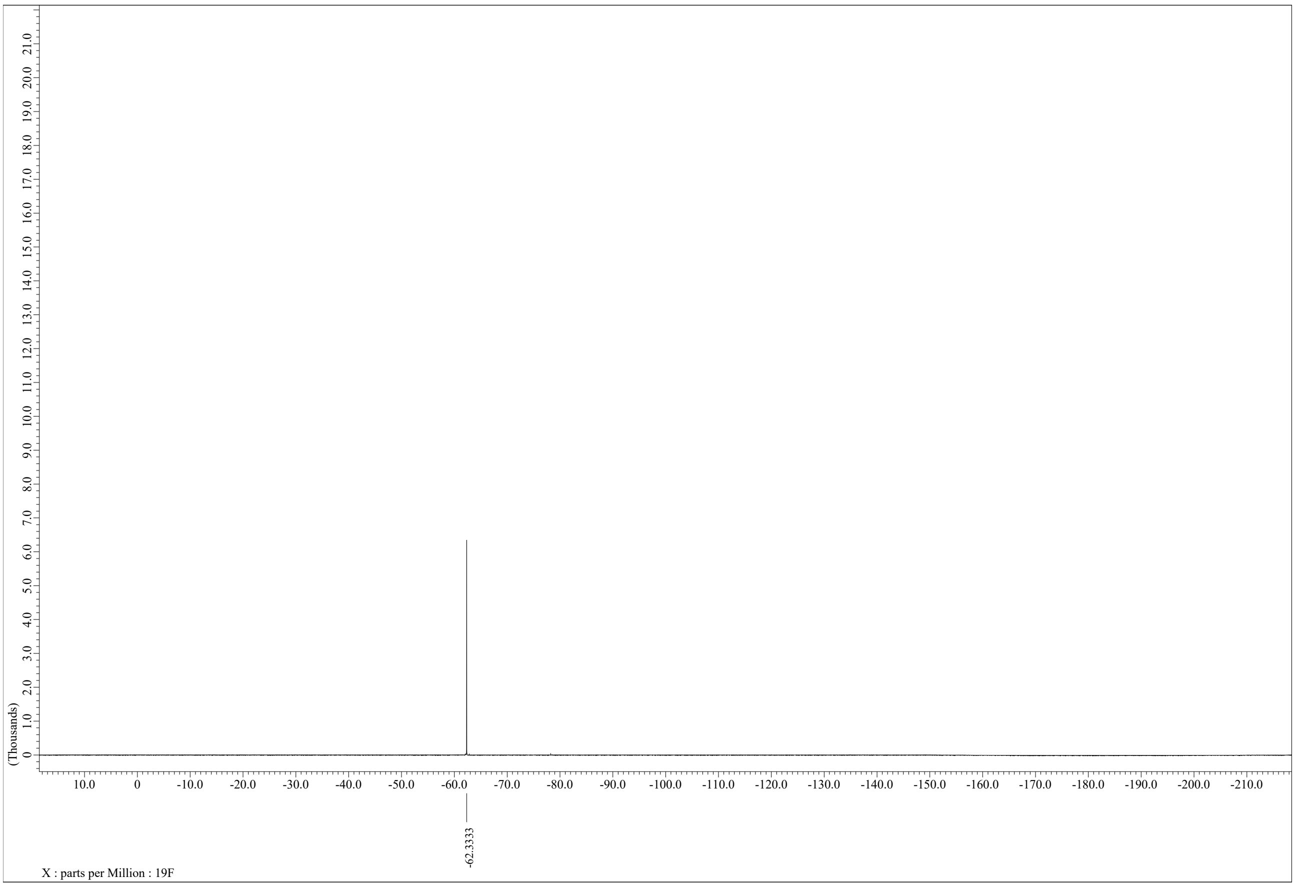
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12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
(Thousands)
10.0
0
-10.0
-20.0
-30.0
-40.0
-50.0
-60.0
-70.0
-80.0
-90.0
-100.0
-110.0
-120.0
-130.0
-140.0
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-190.0
-200.0
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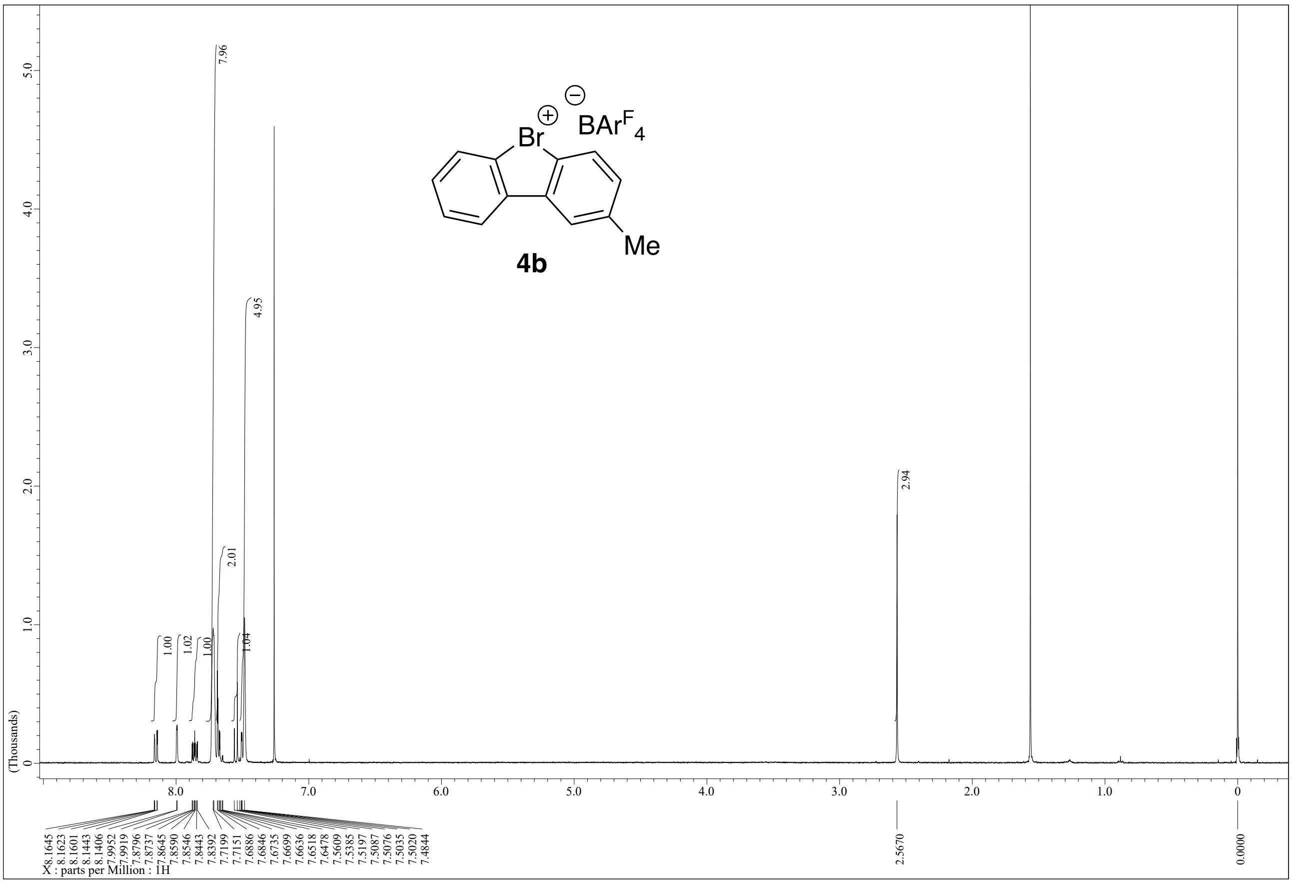
-62.3333
X : parts per Million : 19F


BAr^F_4
Br
Me
4b
(Thousands)
0
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2.0
3.0
4.0
5.0
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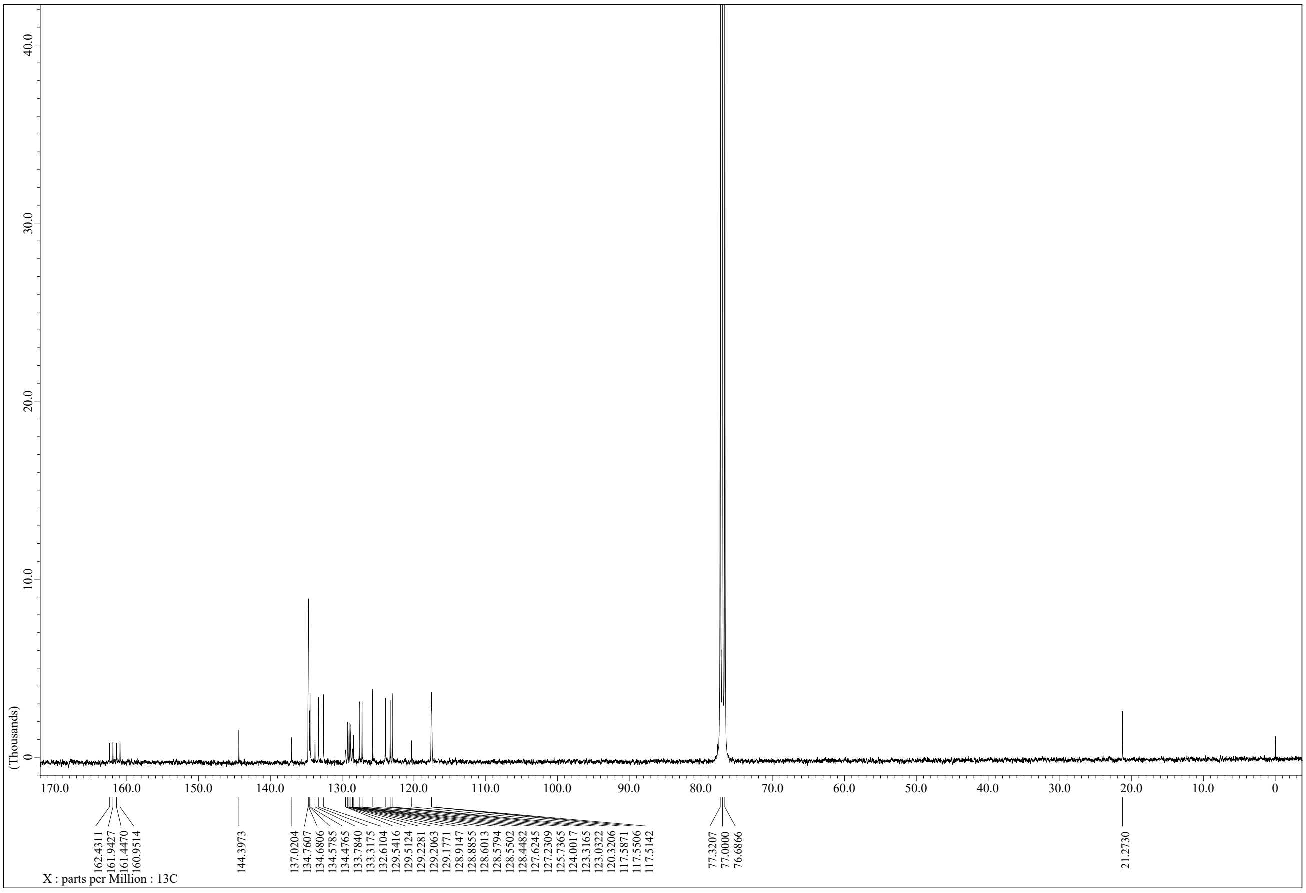
4.95
2.01
1.00
1.02
1.00
1.04
2.94
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.1645
8.1623
8.1601
8.1443
8.1406
7.9952
7.9919
7.8796
7.8737
7.8645
7.8590
7.8546
7.8443
7.8392
7.7199
7.7151
7.6886
7.6846
7.6735
7.6699
7.6636
7.6518
7.6478
7.5609
7.5385
7.5197
7.5087
7.5076
7.5035
7.5020
7.4844
2.5670
0.0000
X : parts per Million : 1H


(Thousands)
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.4311
161.9427
161.4470
160.9514
144.3973
137.0204
134.7607
134.6806
134.5785
134.4765
133.7840
133.3175
132.6104
129.5416
129.5124
129.2281
129.2063
129.1771
128.9147
128.8855
128.6013
128.5794
128.5502
128.4482
127.6245
127.2309
125.7365
124.0017
123.3165
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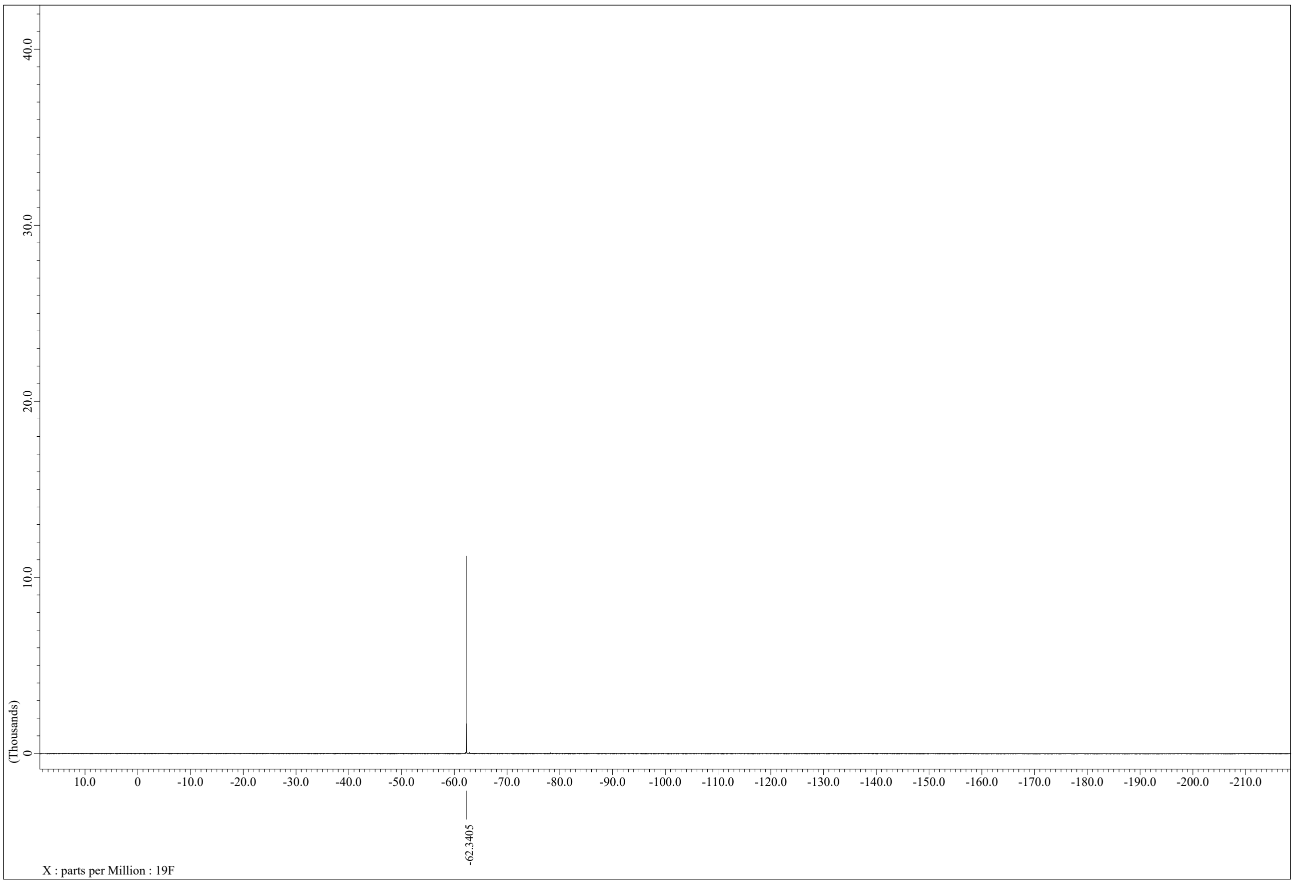
117.5871
117.5506
117.5142
77.3207
77.0000
76.6866
21.2730
X : parts per Million : 13C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10.0
0
(Thousands)
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-10.0
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-30.0
-40.0
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-110.0
-120.0
-130.0
-140.0
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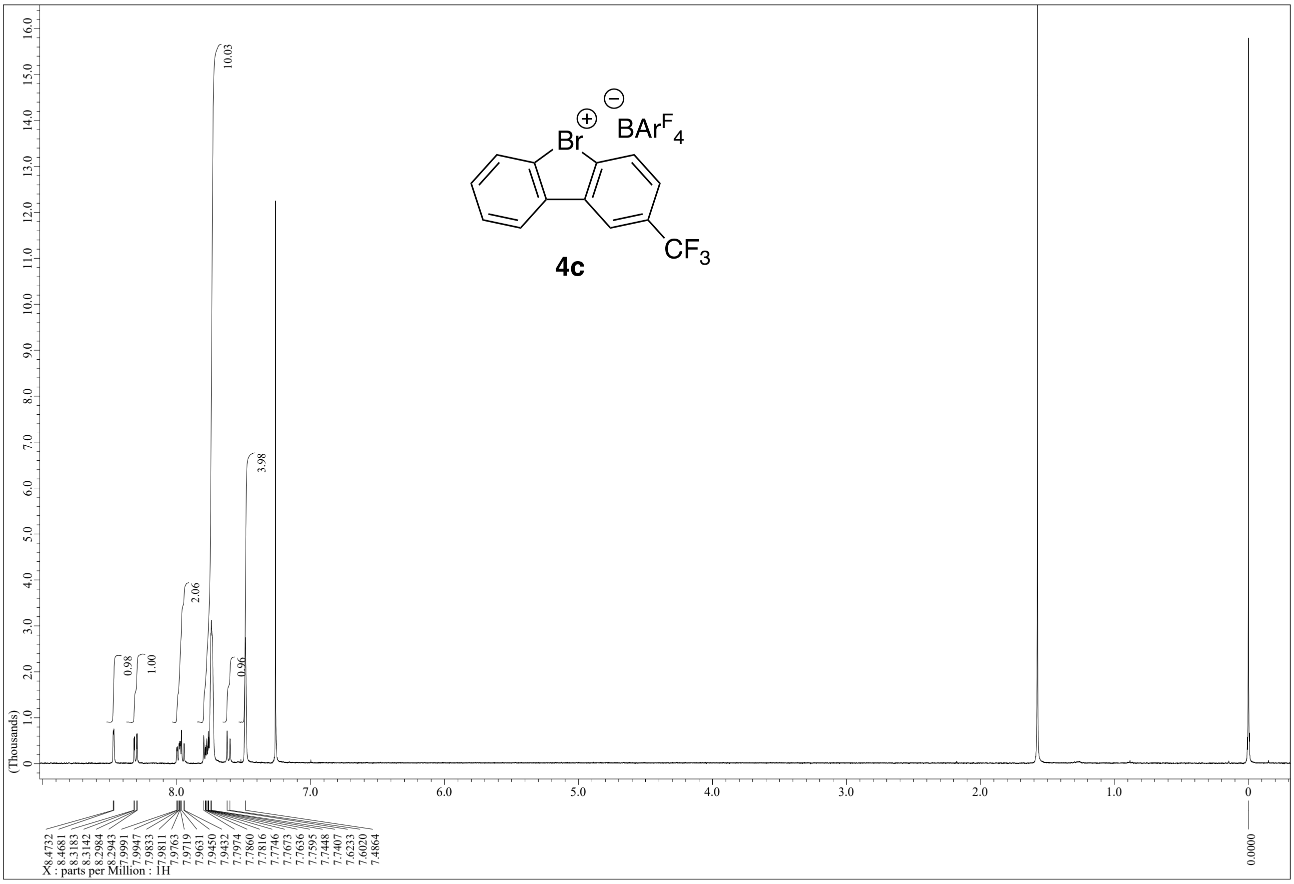
-62.3405
X : parts per Million : 19F


Br
BAr$^F_4$
CF$_3$
4c
(Thousands)
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15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.03
3.98
2.06
0.98
1.00
0.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.4732
8.4681
8.3183
8.3142
8.2984
8.2943
7.9991
7.9947
7.9833
7.9811
7.9763
7.9719
7.9631
7.9450
7.9432
7.7974
7.7860
7.7816
7.7746
7.7673
7.7636
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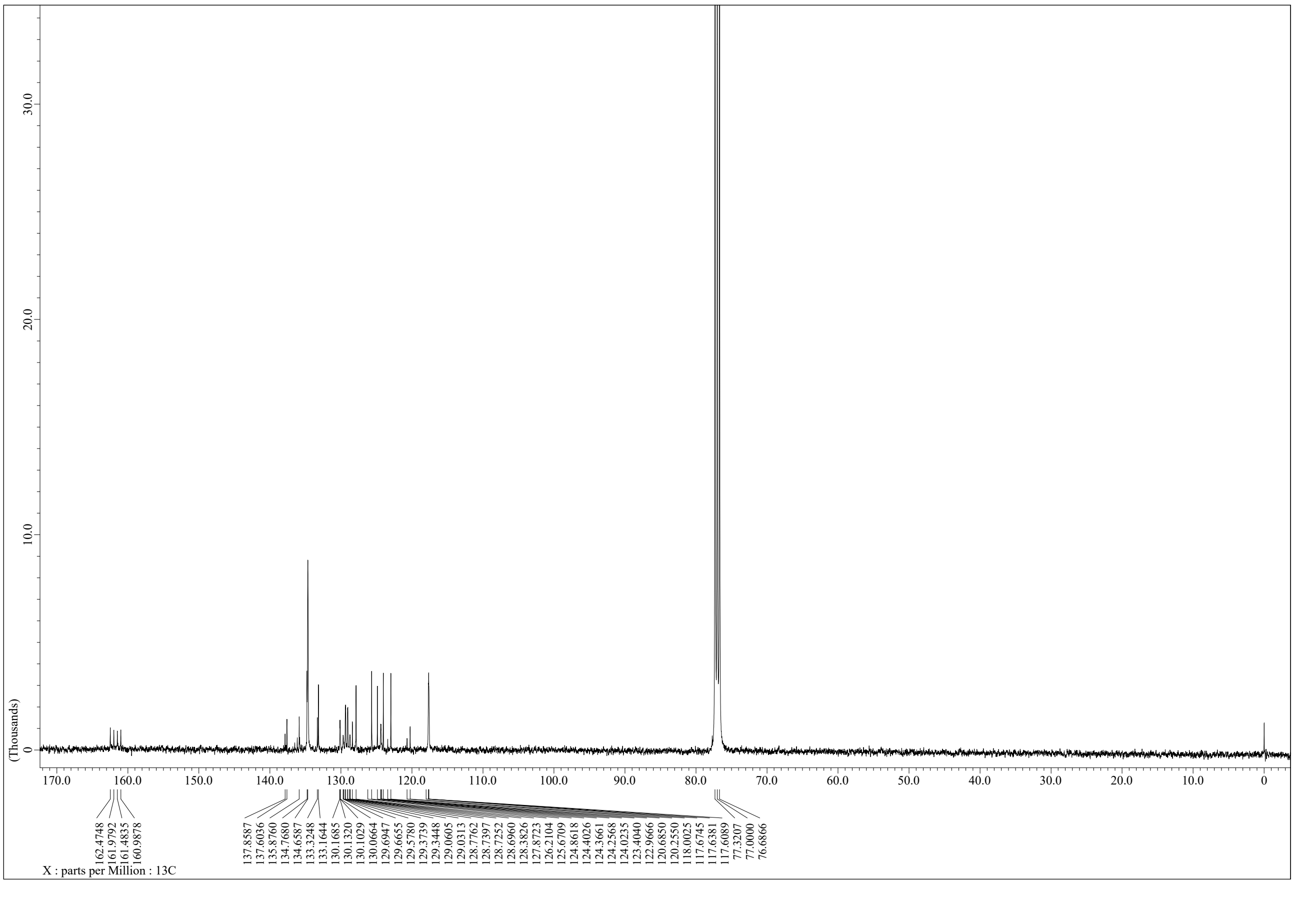
7.7407
7.6233
7.6020
7.4864
0.0000
X : parts per Million : 1H


(Thousands)
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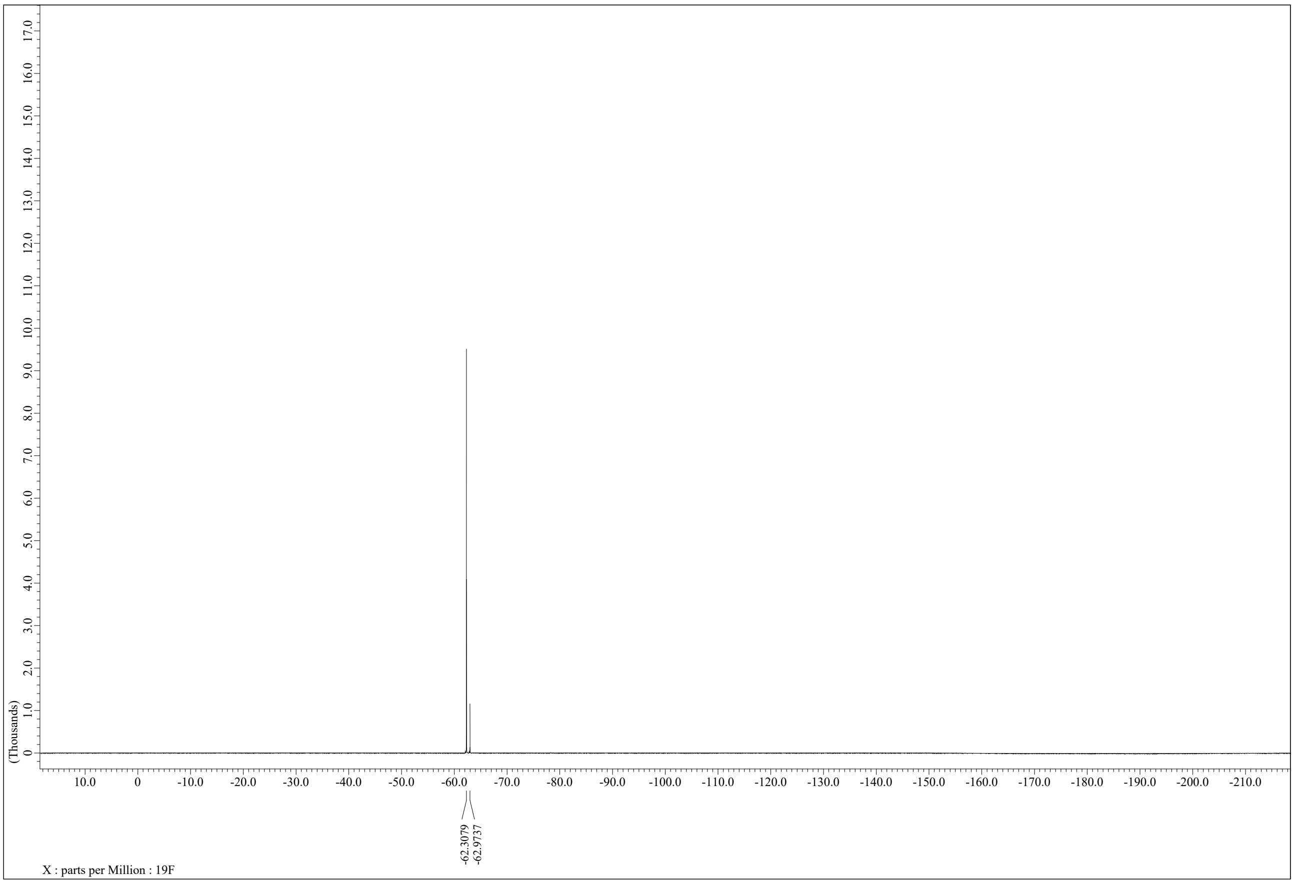
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.4748
161.9792
161.4835
160.9878
137.8587
137.6036
135.8760
134.7680
134.6587
133.3248
133.1644
130.1685
130.1320
130.1029
130.0664
129.6947
129.6655
129.5780
129.3739
129.3448
129.0605
129.0313
128.7762
128.7397
128.7252
128.6960
128.3826
127.8723
126.2104
125.6709
124.8618
124.4026
124.3661
124.2568
124.0235
123.4040
122.9666
120.6850
120.2550
118.0025
117.6745
117.6381
117.6089
77.3207
77.0000
76.6866
X : parts per Million : 13C



(Thousands)
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4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
10.0
0
-10.0
-20.0
-30.0
-40.0
-50.0
-60.0
-70.0
-80.0
-90.0
-100.0
-110.0
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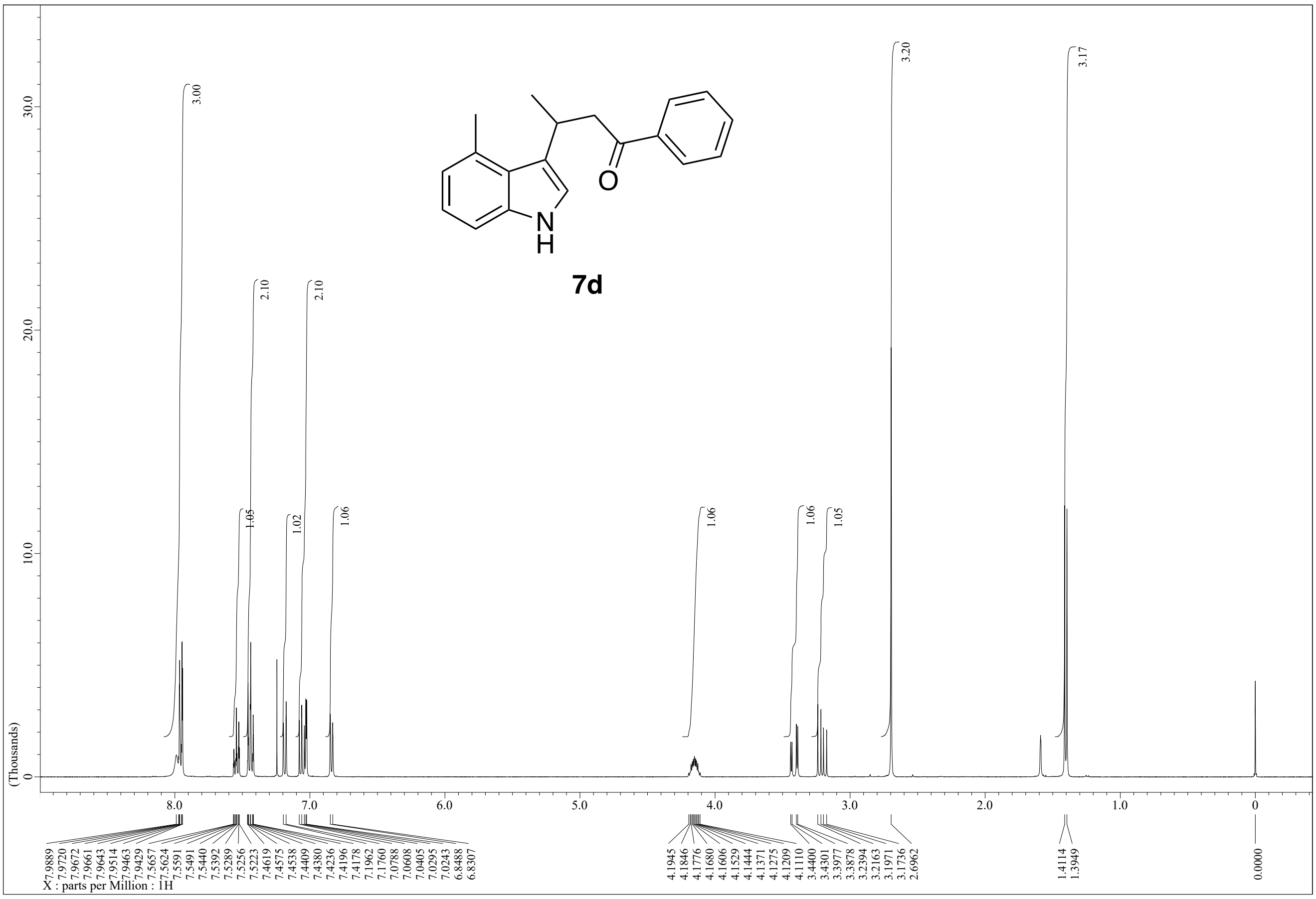
-62.9737
X : parts per Million : 19F



7d
NH
O
(Thousands)
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1.05
2.10
1.02
2.10
1.06
1.06
1.06
1.05
3.20
3.17
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.9889
7.9720
7.9672
7.9661
7.9643
7.9514
7.9463
7.9429
7.5657
7.5624
7.5591
7.5491
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7.5256
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7.4178
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7.0405
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4.1846
4.1776
4.1680
4.1606
4.1529
4.1444
4.1371
4.1275
4.1209
4.1110
3.4400
3.4301
3.3977
3.3878
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3.1971
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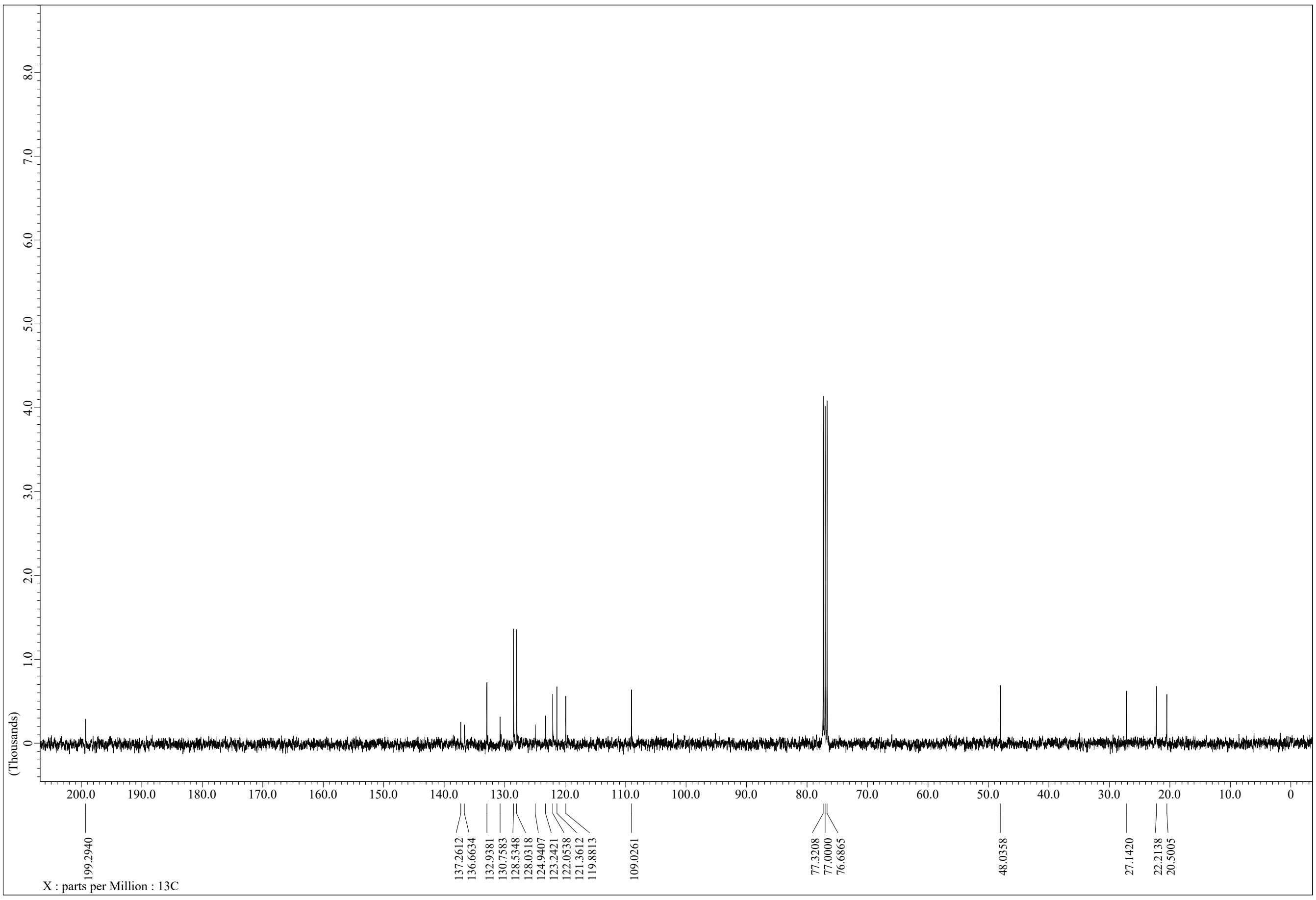
X : parts per Million : 1H



(Thousands)
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2.0
3.0
4.0
5.0
6.0
7.0
8.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
199.2940
137.2612
136.6634
132.9381
130.7583
128.5348
128.0318
124.9407
123.2421
122.0538
121.3612
119.8813
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77.0000
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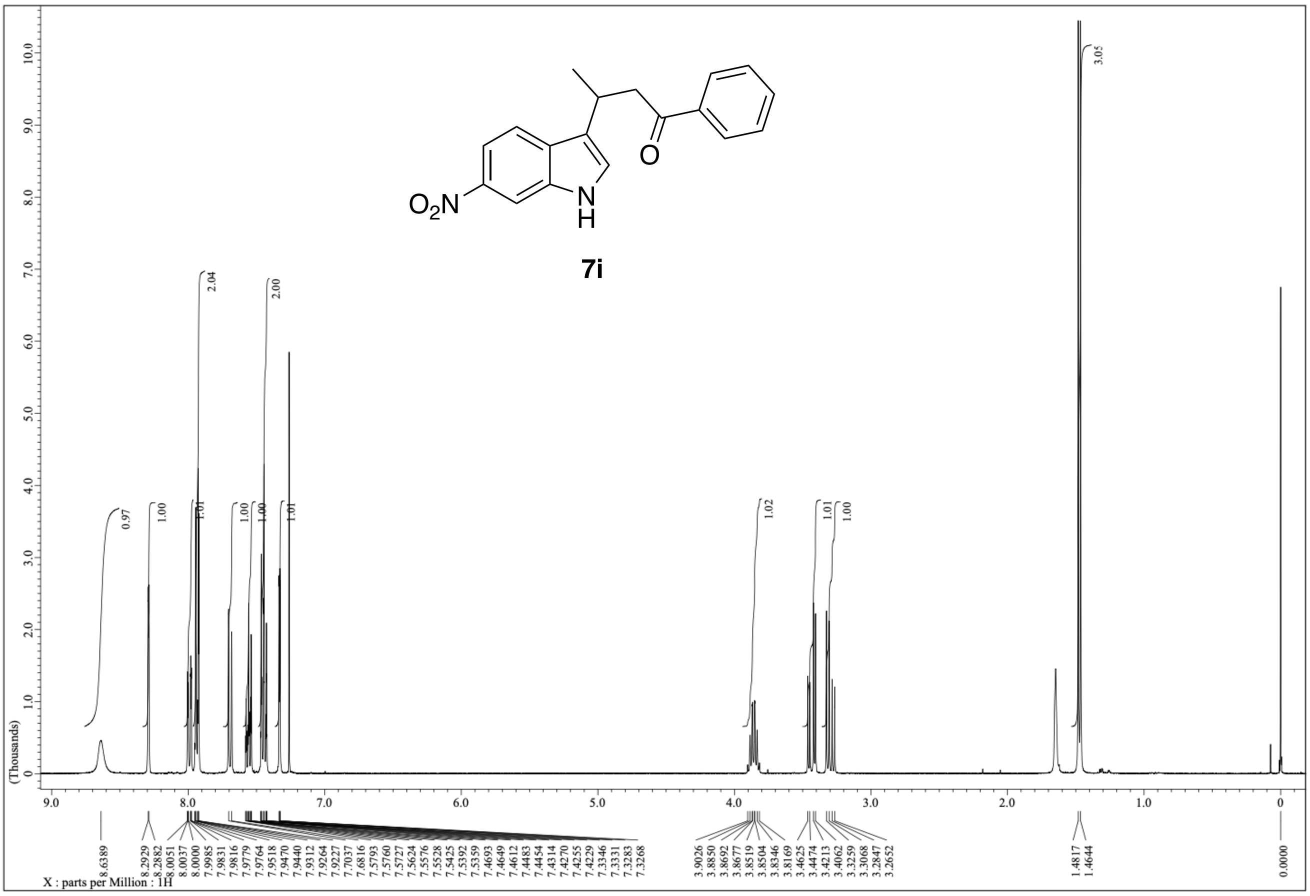
27.1420
22.2138
20.5005
X : parts per Million : 13C


O2N
N
H
O
7i
(Thousands)
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8.0
9.0
10.0
0.97
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1.01
2.04
1.00
1.00
2.00
1.01
1.02
1.01
1.00
3.05
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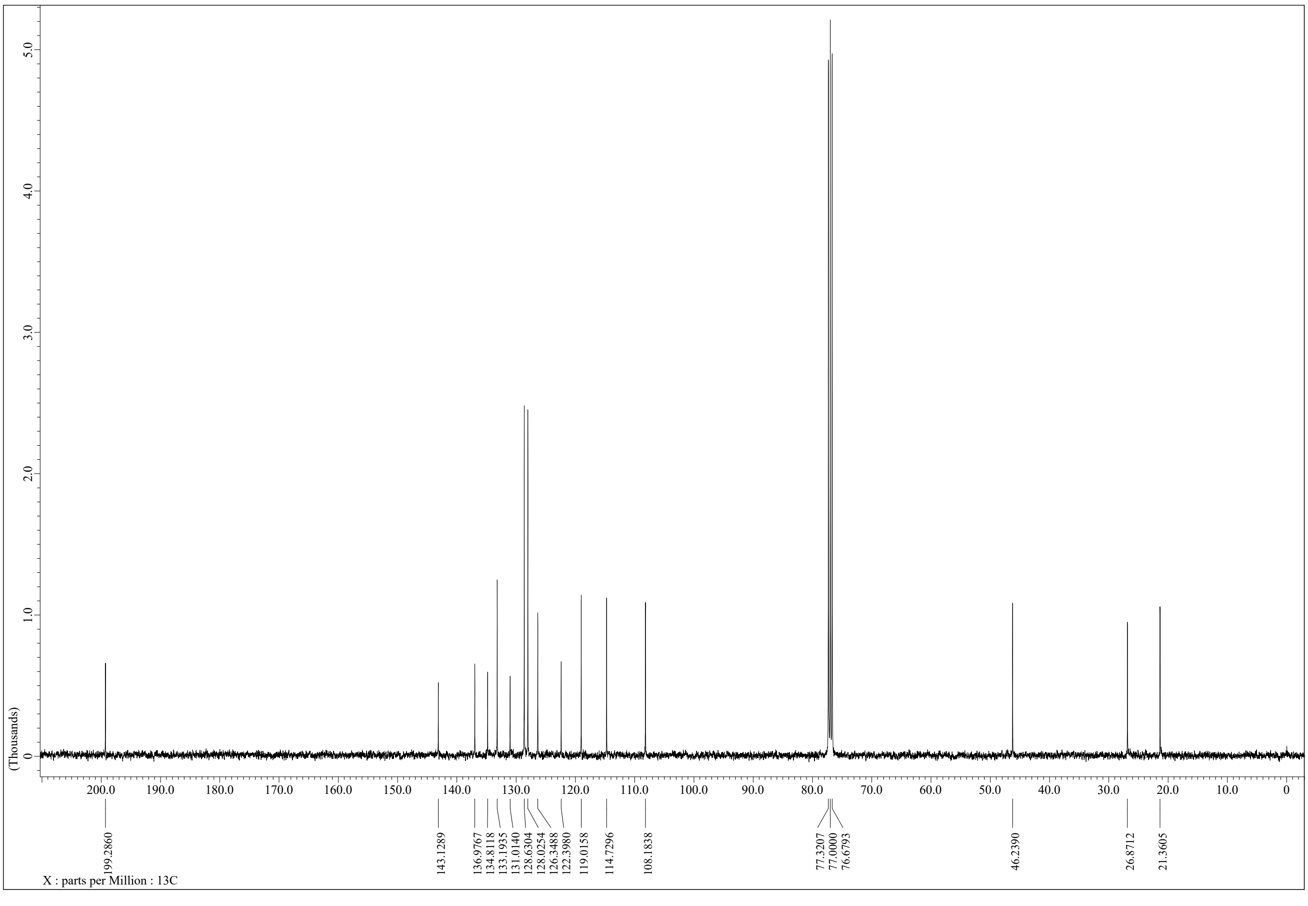
X : parts per Million : 1H


(Thousands)
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
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40.0
30.0
20.0
10.0
0
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136.9767
134.8118
133.1935
131.0140
128.6304
128.0254
126.3488
122.3980
119.0158
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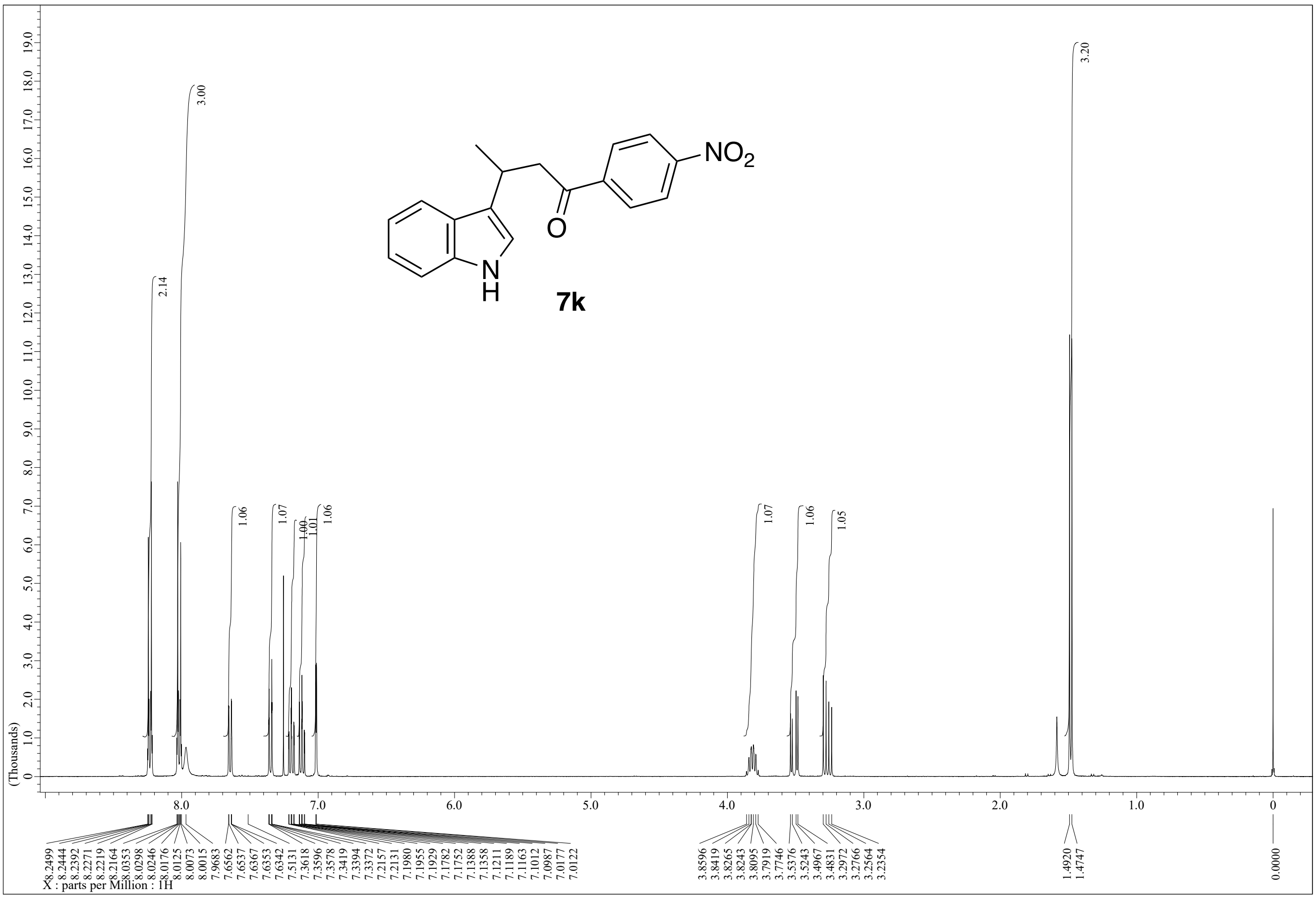
77.3207
77.0000
76.6793
46.2390
26.8712
21.3605
X : parts per Million : 13C


7k
NO2
O
N
H
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19.0
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1.07
1.00
1.01
1.06
1.07
1.06
1.05
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8.0015
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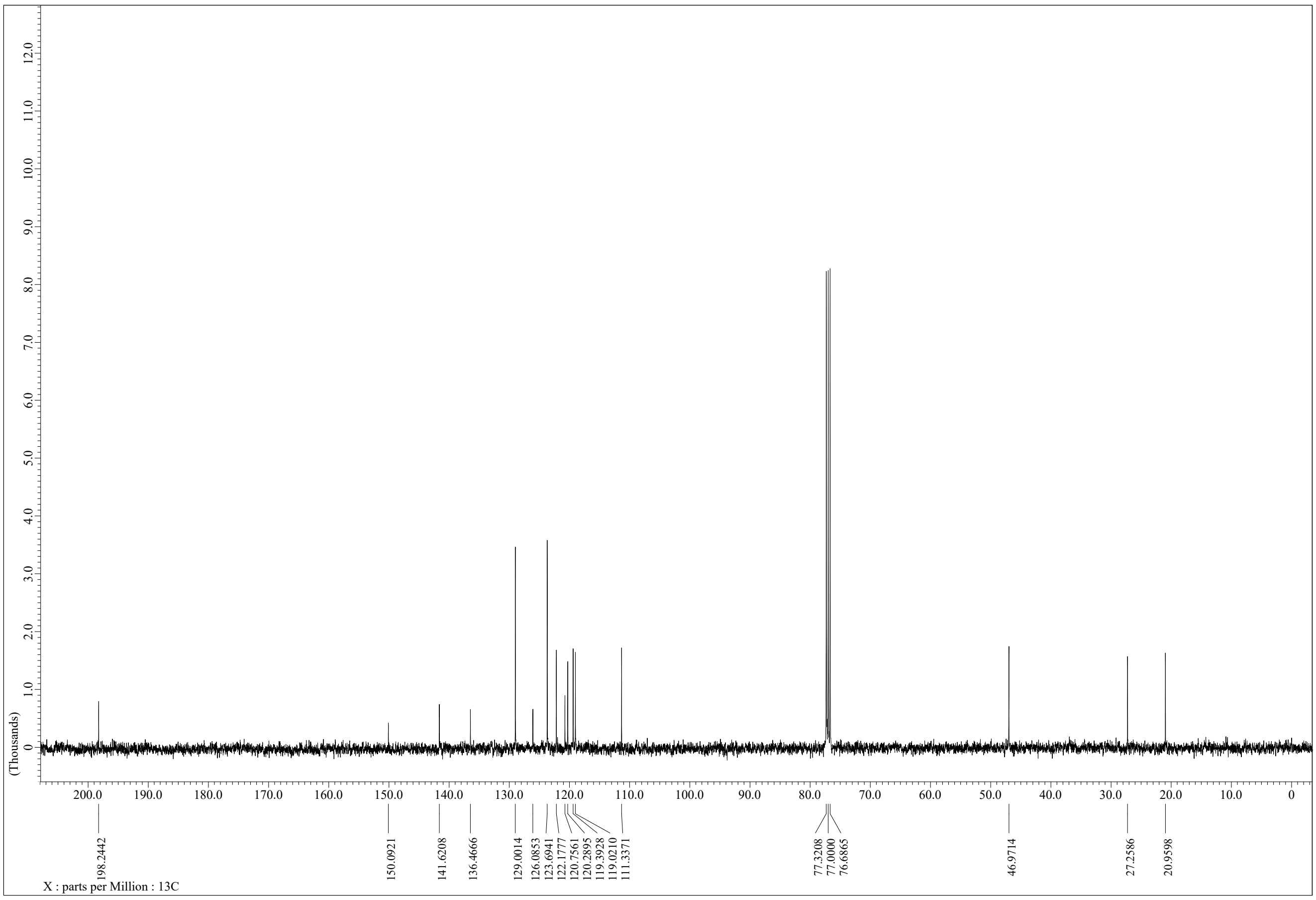
X : parts per Million : 1H


(Thousands)
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10.0
11.0
12.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
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90.0
80.0
70.0
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120.7561
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X : parts per Million : 13C